AIPMT 2014
Topper Interview
Lovedeep S. Dhingra

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Vol. XXIII No. 7 July 2014

Corporate Office :
Plot 99, Sector 44 Institutional area,
Gurgaon -122 003 (HR). Tel : 0124-4951200
e-mail : info@mtg.in website : www.mtg.in

Regd. Office
406, Taj Apartment, Near Safdarjung Hospital,
Ring Road, New Delhi - 110029.

Managing Editor : Mahabir Singh
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Contents

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Editor : Anil Ahlawat

editorial

The Battle Against Diabetes Continues

Diabetes patients have sugar in their blood above the permitted level. This becomes a killer disease unless detected in time and proper medicines are taken.

Normally a sample of blood can give indications of the disease by measuring sugar in blood. Normal methods used in hospitals take time. Taking samples many times increases the risk of contamination.

Instead of taking samples of blood, if one can get the results by studying saliva, it is very much safer. Further, one of the most sensitive techniques, namely spectrometry was tried. One has grating spectrometers and in X-Rays, crystals such as mica serve as the purpose of a grating.

Methods of spectroscopy are extremely sensitive. Emission, absorption techniques, atomic, molecular, infrared spectrometers and X-Ray spectrometers are well-known. There are also sister-techniques for dispersion, well known for chemists. This is chromatography.

In the present discovery, blood samples are not taken but only saliva. A nanoscale interferometer is made by coating a thin layer of silver on the surface of one inch square of quartz.

The layer of silver has etched on the surface, a nanoscale interferometer by etching thousands of slits with grooves on each side. The width of the groove is 100 nanometers. With this high precision grating, one can determine in saliva even sugar 100 times lower than in blood.

To summarise, one has developed a new application of sensitive spectrometer. Now this method has to be further developed by mathematical means which have been able to get over many problems such as differences in matrix and background.

Anil Ahlawat
Editor

AIPMT 2014
Topper Interview

AIPMT 2014 Topper Interview : How LOVEDEEP SINGH DHINGRA scored 680 out of 720?

AIPMT 2014 Topper Lovedeep Singh Dhingra secured 680 out of total 720 marks in AIPMT 2014 Exam. The Jalandhar boy scored perfect 180 marks in Physics and fetched an overall score of 680 to be ranked second in AIPMT 2014. Despite being a student with extraordinary intelligence, he has a passion for doing magic tricks with family and friends. His parents, both of whom are doctors, were very helpful during the last stages of preparation.

Here, Lovedeep talks about his AIPMT preparation strategy, future dreams and his love for movies.

Lovedeep Singh Dhingra

Congratulations Lovedeep for scoring 680 in AIPMT 2014!

Thanks a lot for your wishes.

What is your overall and subject-wise score in AIPMT 2014?

My overall score in AIPMT 2014 is 680. I got 100% marks in Physics, i.e. 180 out of 180. In Chemistry, I scored 170 out of 180 and 330 in Biology out of 360.

How did you prepare for AIPMT 2014? Which books did refer to?

I just followed my coaching experts' advice. I found NCERT books to be very helpful, especially Biology and Chemistry. Most of the Biology section was from NCERT book. Around 95% Biology section in AIPMT exam will come from NCERT books only. For Physics, I focused on strengthening my concepts. I studied from the notes given in coaching classes.

How much time did you devote to your studies during AIPMT 2014 preparation?

I did not study for prolonged hours. I just focused on completing my target syllabus, which I decided for myself when I sat for studying. I never decided how many hours I would devote, but I used to decide what all topics I will be covering in one sitting. I am not a bookworm at all.

Besides studies, what do you do? What do you do in your leisure time?

Showing magic tricks to my friends and family is a great source of recreation for me. I have very keen interest in learning unique magic tricks from television and books. Earlier, I was a bit active on Facebook, but left that completely during the preparation time.

Which is your favorite movie? Which movie did you watch last?

There is not any particular movie that I like the most. I watch English, Hindi and Punjabi movies. The last movie I watched was Die Hard, and that too thrice!

Contd. on page no. 8

CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 12

JEE MAIN/PMTS

1. An organic compound *A*, containing C, H, N and O, on analysis gives 49.32% carbon, 9.59% hydrogen and 19.18% nitrogen. *A* on boiling with NaOH gives off NH_3 and a salt which on acidification gives a monobasic nitrogen free acid *B*. The silver salt of *B* contains 59.67% silver. Structures of *A* and *B* are respectively
   (a) C_2H_5COOH, $CH_3CH_2CONH_2$
   (b) $CH_3CONHCH_3$, CH_3COOH
   (c) $CH_3CH_2CONH_2$, C_2H_5COOH
   (d) $CH_3CH_2CH_2NH_2$, $C_2H_5COOCH_3$

2. Which of the following order is incorrect?
   (a) $CCl_4 < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$ – extent of hydrolysis
   (b) $SiO_2 < CO_2 < N_2O_5 < SO_3$ – acidic strength
   (c) $HClO < HClO_2 < HClO_3 < HClO_4$ – thermal stability
   (d) $H_2O < H_2S < H_2Se < H_2Te$ – pK_a values

3. The $[H^+]$ in 0.2 M solution of formic acid is 6.4×10^{-3} mole litre^{-1}. To this solution sodium formate is added so as to adjust the concentration of sodium formate to one mole litre^{-1}. pH of this solution is

   Given : K_a for HCOOH is 2.4×10^{-4} and degree of dissociation of HCOONa is 0.75.
   (a) 4.19 (b) 7.82
   (c) 5.20 (d) 2.45

4. If the de Broglie wavelength of a particle of mass *m* is 100 times its velocity, then its value in terms of its mass (*m*) and Planck's constant (*h*) is
   (a) $\frac{1}{10}\sqrt{\frac{m}{h}}$ (b) $10\sqrt{\frac{h}{m}}$
   (c) $\frac{1}{10}\sqrt{\frac{h}{m}}$ (d) $10\sqrt{\frac{m}{h}}$

5. Arrange the following ions in the order of decreasing *X*–O bond length where *X* is the central atom
   (a) ClO_4^-, SO_4^{2-}, PO_4^{3-}, SiO_4^{4-}
   (b) SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^-
   (c) SiO_4^{4-}, PO_4^{3-}, ClO_4^-, SO_4^{2-}
   (d) SO_4^{2-}, SiO_4^{4-}, PO_4^{3-}, ClO_4^-

JEE ADVANCED

6. The correct stability order of the following resonance structures is
   (I) $H_2C = \overset{+}{N} = N^-$ (II) $H_2\overset{+}{C} — N = N^-$
   (III) $H_2\bar{C} — \overset{+}{N} \equiv N$ (IV) $H_2\bar{C} — N = \overset{+}{N}$

(a) I > II > IV > III (b) I > III > II > IV

(c) II > I > III > IV (d) III > I > IV > II

COMPREHENSION

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below.

(a) Distillation
(b) Liquation
(c) Electrolysis
(d) Zone refining
(e) Vapour phase refining
(f) Chromatographic methods

7. In the purification of Zr and Ti, which of the following is/are true?

(a) $Zr_{(s)} + 2I_{2(g)} \rightarrow ZrI_{4(g)}$;
The pure Zr is deposited on W.

(b) $Ti_{(s)} + 2I_{2(g)} \rightarrow TiI_{4(g)}$;
The pure Ti is deposited on W.

(c) $Zr_{(s)} + 2I_{2(g)} \rightarrow ZrI_{4(s)}$;
ZrI_4 is reduced to ZrI_2.

(d) Both (a) and (b) are correct.

8. For which of the given sulphides autoreduction is not applicable?

(a) Cu_2S (b) PbS
(c) FeS (d) Sb_2S_3

INTEGER VALUE

9. How many of the following colloidal systems are sols?
Butter, paints, insecticide sprays, pumice stone, coloured glasses, muddy water, cell fluids

10. Amongst the following, the total number of nucleophiles is
SO_3, NH_2^-, R^-, H_2O, OR^-, ROH, $AlCl_3$, H^-, BF_3

Solution Senders of Chemistry Musing

SET 11

1. Arun Nayan, Ghazipur (UP)

SET 10

1. Nesa Mirza, Kolkata (West Bengal)
2. Atul Pratap Singh, Ghazipur (UP)
3. S Ravi Sankar, Pondicherry

Contd. from page no. 4

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What about your family? How did they help you?

My mother and father are doctors. They inspired and stood by me throughout my preparation time. There was no pressure from their side at all. Thankfully, both my parents were supportive and showed a lot of confidence in me.

What is your message to the AIPMT aspirants?

I would like to suggest that they should experiment. For instance, if you feel like studying at midnight, then do it. Study whenever you want to. Solving sample papers and mock test papers will help you a lot in giving the idea about the actual paper.

Now you have cracked AIPMT 2014, which Medical College would you like to opt for?

My first preference is All India Institute of Medical Sciences (AIIMS). Maulana Azad Medical College is the next on my list. I am hoping for the best!

All the best for your AIPMT 2014 dream Medical College!

Thanks a lot!

Courtesy : careers360.com

SOLVED PAPER 2014

JEE Advanced

PAPER-I

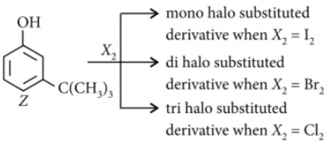
SECTION-I

One or More Than One Options Correct Type

This section contains 10 multiple choice type questions. Each question has four choices (a), (b), (c) and (d) out of which ONE or MORE THAN ONE are correct.

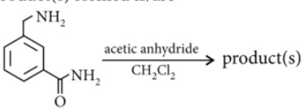
1. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are
   (a) *tert*-butanol and 2-methylpropan-2-ol
   (b) *tert*-butanol and 1, 1-dimethylethan-1-ol
   (c) *n*-butanol and butan-1-ol
   (d) *iso*-butyl alcohol and 2-methylpropan-1-ol.

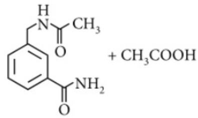
2. The reactivity of compound Z with different halogens under appropriate conditions is given below :

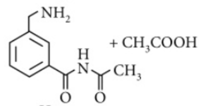


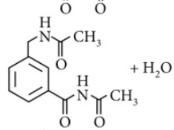
   The observed pattern of electrophilic substitution can be explained by
   (a) the steric effect of the halogen
   (b) the steric effect of the *tert*-butyl group
   (c) the electronic effect of the phenolic group
   (d) the electronic effect of the *tert*-butyl group.

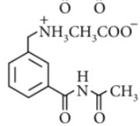
3. In the reaction shown below, the major product(s) formed is/are



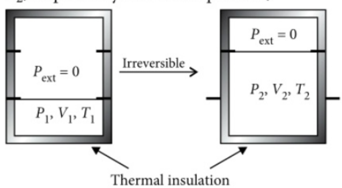
(a) 

(b) 

(c) 

(d) 

4. An ideal gas in a thermally insulated vessel at internal pressure = P_1, volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of gas are P_2, V_2 and T_2, respectively. For this expansion,



(a) $q = 0$ (b) $T_2 = T_1$
(c) $P_2V_2 = P_1V_1$ (d) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

5. Hydrogen bonding plays a central role in the following phenomena :
(a) Ice floats in water.
(b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions.
(c) Formic acid is more acidic than acetic acid.
(d) Dimerisation of acetic acid in benzene.

6. In a galvanic cell, the salt bridge
(a) does not participate chemically in the cell reaction
(b) stops the diffusion of ions from one electrode to another
(c) is necessary for the occurrence of the cell reaction
(d) ensures mixing of the two electrolytic solutions.

7. Upon heating with Cu_2S, the reagent(s) that give copper metal is/are
(a) $CuFeS_2$ (b) CuO
(c) Cu_2O (d) $CuSO_4$

8. The correct statement(s) for orthoboric acid is/are
(a) it behaves as a weak acid in water due to self ionization
(b) acidity of its aqueous solution increases upon addition of ethylene glycol
(c) it has a three dimensional structure due to hydrogen bonding
(d) it is a weak electrolyte in water.

9. For the reaction :
$I^- + ClO_3^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$
The correct statement(s) in the balanced equation is/are
(a) stoichiometric coefficient of HSO_4^- is 6
(b) iodide is ozidized
(c) sulphur is reduced
(d) H_2O is one of the products.

10. The pair(s) of reagents that yield paramagnetic species is/are
(a) Na and excess of NH_3
(b) K and excess of O_2
(c) Cu and dilute HNO_3
(d) O_2 and 2-ethylanthraquinol.

SECTION-2

One Integer Value Correct Type

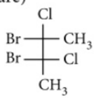
This section contains 10 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive).

11. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$ (NOTE : stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are

12. A list of species having the formula XZ_4 is given below.
XeF_4, SF_4, SiF_4, BF_4^-, BrF_4^-, $[Cu(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$.
Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

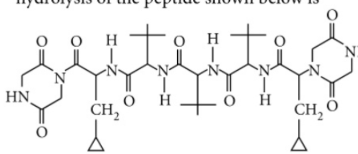
13. Among PbS, CuS, HgS, MnS, Ag_2S, NiS, CoS, Bi_2S_3 and SnS_2, the total number of BLACK coloured sulphides is

14. The total number(s) of stable conformers with non-zero dipole moment for the following compound is (are)



15. Consider the following list of reagents :
Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3 and $Na_2S_2O_3$. The total number of reagents that can oxidise aqueous iodide to iodine is

16. The total number of distinct naturally occurring amino acids obtained by complete acidic hydrolysis of the peptide shown below is



17. In an atom, the total number of electrons having quantum numbers, $n = 4$, $|m_l| = 1$ and $m_s = -1/2$ is

18. If the value of Avogadro number is $6.023 \times 10^{23}\ mol^{-1}$ and the value of Boltzmann constant is $1.380 \times 10^{-23}\ J\ K^{-1}$, then the number of significant digits in the calculated value of the universal gas constant is

19. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g mL^{-1}. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is

20. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is

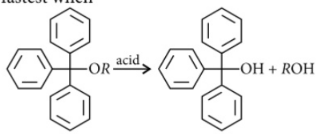
PAPER-II

SECTION-I

Only One Option Correct Type

This section contains 10 multiple choice questions. Each question has four choices (a), (b), (c) and (d) out of which ONLY ONE option is correct.

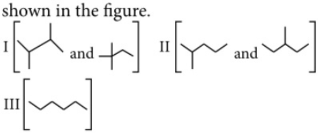
1. The acidic hydrolysis of ether (X) shown below is fastest when



[X]

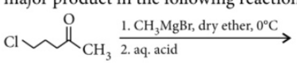
(a) one phenyl group is replaced by a methyl group
(b) one phenyl group is replaced by a *para*-methoxyphenyl group
(c) two phenyl groups are replaced by two *para*-methoxyphenyl groups
(d) no structural change is made to X.

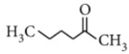
2. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.

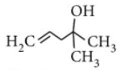


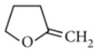
The correct order of their boiling point is
(a) I > II > III
(b) III > II > I
(c) II > III > I
(d) III > I > II

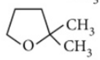
3. The major product in the following reaction is



(a) 

(b) 

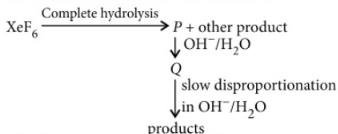
(c) 

(d) 

4. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a
(a) reducing agent, oxidising agent
(b) reducing agent, reducing agent
(c) oxidising agent, oxidising agent
(d) oxidising agent, reducing agent.

5. The product formed in the reaction of $SOCl_2$ with white phosphorous is
(a) PCl_3
(b) SO_2Cl_2
(c) SCl_2
(d) $POCl_3$

6. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is



(a) 0
(b) 1
(c) 2
(d) 3

7. For the identification of β-naphthol using dye test, it is necessary to use
(a) dichloromethane solution of β-naphthol
(b) acidic solution of β-naphthol
(c) neutral solution of β-naphthol
(d) alkaline solution of β-naphthol.

8. For the elementary reaction $M \rightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is

(a) 4 (b) 3
(c) 2 (d) 1

9. For the process

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

at $T = 100$ °C and 1 atmosphere pressure, the correct choice is

(a) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$
(b) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$
(c) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$
(d) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

10. Assuming $2s$-$2p$ mixing is not operative, the paramagnetic species among the following is
(a) Be_2 (b) B_2
(c) C_2 (d) N_2

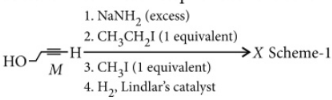
SECTION-2

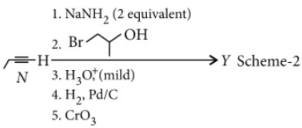
Comprehension Type (Only One Option Correct)

This section contains 3 paragraphs, each describing theory, experiments, data etc. Six questions relate to the three paragraphs with two questions on each paragraph. Each question has only one correct answer among the four given options (a), (b), (c) and (d).

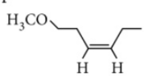
Paragraph for Questions 11 and 12

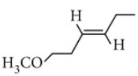
Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both the schemes.

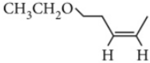


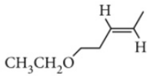


11. The product X is

(a) 

(b) 

(c) 

(d) 

12. The correct statement with respect to product Y is
(a) it gives a positive Tollens test and is a functional isomer of X.
(b) it gives a positive Tollens test and is a geometrical isomer of X.
(c) it gives a positive iodoform test and is a functional isomer of X.
(d) it gives a positive iodoform test and is a geometrical isomer of X.

Paragraph for Questions 13 and 14

An aqueous solution of metal ion $M1$ reacts separately with reagents Q and R in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion $M2$ always forms tetrahedral complexes with these reagents. Aqueous solution of $M2$ on reaction with reagent S gives white precipitate which dissolves in excess of S. The reactions are summarized in the scheme given below :

SCHEME :

$$\text{Tetrahedral} \xleftarrow[\text{excess}]{Q} M1 \xrightarrow[\text{excess}]{R} \text{Square planar}$$

$$\text{Tetrahedral} \xleftarrow[\text{excess}]{Q} M2 \xrightarrow[\text{excess}]{R} \text{Tetrahedral}$$

$$M2 \xrightarrow{S,\ \text{stoichiometric amount}} \text{White precipitate} \xrightarrow[\text{excess}]{S} \text{precipitate dissolves}$$

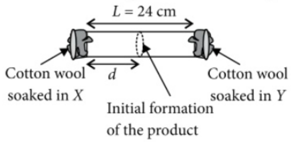
13. $M1$, Q and R, respectively are
(a) Zn^{2+}, KCN and HCl
(b) Ni^{2+}, HCl and KCN
(c) Cd^{2+}, KCN and HCl
(d) Co^{2+}, HCl and KCN

14. Reagent S is
(a) $K_4[Fe(CN)_6]$ (b) Na_2HPO_4
(c) K_2CrO_4 (d) KOH

Paragraph for Questions 15 and 16

X and Y are two volatile liquids with molar weights of 10 g mol^{-1} and 40 g mol^{-1} respectively. Two cotton

plugs, one soaked in X and the other soaked in Y, are simultaneously placed at the ends of a tube of length $L = 24$ cm, as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K. Vapours of X and Y react to form a product which is first observed at a distance d cm from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.



15. The value of d in cm (shown in the figure), as estimated from Graham's law, is

(a) 8 (b) 12
(c) 16 (d) 20

16. The experimental value of d is found to be smaller than the estimate obtained using Graham's law. This is due to

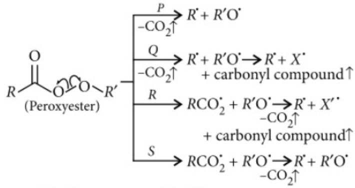
(a) larger mean free path of X as compared to that of Y
(b) larger mean free path for Y as compared to that of X
(c) increased collision frequency of Y with the inert gas as compared to that of X with the inert gas
(d) increased collision frequency of X with the inert gas as compared to that of Y with the inert gas.

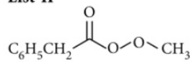
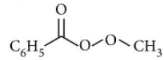
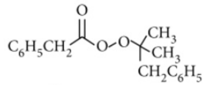
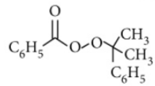
SECTION-3

Matching List Type (Only One Option Correct)

This section contains four questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (a), (b), (c) and (d) out of which one is correct.

17. Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from List I with an appropriate structure from List II and select the correct answer using the code given below the lists.

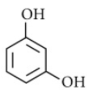


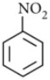
List-I	List-II
(P) Pathway P	1. 
(Q) Pathway Q	2. 
(R) Pathway R	3. 
(S) Pathway S	4. 

Code :

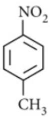
	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

18. Match the four starting materials (P, Q, R, S) given in List-I with the corresponding reaction schemes (I, II, III, IV) provided in List-II and select the correct answer using the code given below the lists.

List-I	List-II
(P) H≡H	1. **Scheme I** (i) $KMnO_4$, HO^-, heat (ii) H^+, H_2O (iii) $SOCl_2$ (iv) NH_3 $? \longrightarrow C_7H_6N_2O_3$
(Q) 	2. **Scheme II** (i) Sn/HCl (ii) CH_3COCl (iii) conc. H_2SO_4 (iv) HNO_3 (v) dil. H_2SO_4, heat (vi) HO^- $? \longrightarrow C_6H_6N_2O_2$

(R) 

3. **Scheme III**
(i) red hot iron, 873 K
(ii) fuming HNO_3, H_2SO_4, heat
(iii) $H_2S.NH_3$
(iv) $NaNO_2$, H_2SO_4
(v) hydrolysis
$? \longrightarrow C_6H_5NO_3$

(S) 

4. **Scheme IV**
(i) conc.H_2SO_4, 60°C
(ii) conc. HNO_3, conc. H_2SO_4
(iii) dil. H_2SO_4, heat
$? \longrightarrow C_6H_5NO_4$

Code :

	P	Q	R	S
(a)	1	4	2	3
(b)	3	1	4	2
(c)	3	4	2	1
(d)	4	1	3	2

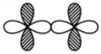
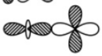
19. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists.
{en = $H_2NCH_2CH_2NH_2$; atomic numbers : Ti = 22; Cr = 24; Co = 27; Pt = 78}

List-I	List-II
(P) $[Cr(NH_3)_4Cl_2]Cl$	1. Paramagnetic and exhibits ionisation isomerism
(Q) $[Ti(H_2O)_5Cl](NO_3)_2$	2. Diamagnetic and exhibits *cis-trans* isomerism
(R) $[Pt(en)(NH_3)Cl]NO_3$	3. Paramagnetic and exhibits *cis-trans* isomerism
(S) $[Co(NH_3)_4(NO_3)_2]NO_3$	4. Diamagnetic and exhibits ionisation isomerism

Code :

	P	Q	R	S
(a)	4	2	3	1
(b)	3	1	4	2
(c)	2	1	3	4
(d)	1	3	4	2

20. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists.

List-I	List-II
(P) 	1. $p-d\pi$ antibonding
(Q) 	2. $d-d\sigma$ bonding
(R) 	3. $p-d\pi$ bonding
(S) 	4. $d-d\sigma$ antibonding

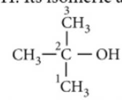
Code :

	P	Q	R	S
(a)	2	1	3	4
(b)	4	3	1	2
(c)	2	3	1	4
(d)	4	1	3	2

SOLUTIONS

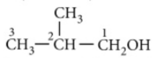
PAPER-I

1. **(a, c, d) :** $C_4H_{10}O$ is a monohydric alcohol, *i.e.*, C_4H_9OH. Its isomeric alcohols are

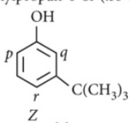
(a) 

2-Methylpropan-2-ol (*tert*-butanol)

(c) $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2OH$
Butan-1-ol (*n*-butanol)

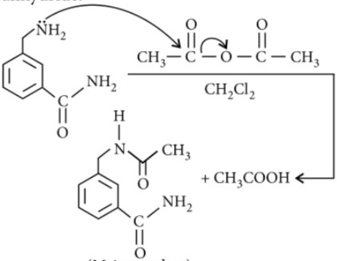
(d) 

2-Methylpropan-1-ol (*iso*-butyl alcohol)

2. **(a, b, c) :** 

p, q and r are suitable positions as per electronic effect of –OH group. Due to steric effect of the *tert*-butyl group, the bulky electrophiles are less likely to attack positions q and r. Hence, position p is suitable for I_2, positions p and r are suitable for Br_2 and Cl_2 being smaller can attack all p, q and r positions.

3. **(a) :** Acetylation takes place when amine (not amide) combines with acetyl chloride or acetic anhydride.



(Major product)

4. **(a, b, c) :** Since vessel is thermally insulated, *i.e.* the process is adiabatic hence, $q = 0$
Also, $P_{ext} = 0$, hence $w = 0$
From 1st law of thermodynamics, $\Delta E = q + w$
$\therefore \quad \Delta E = 0$ (for ideal gas)
$\therefore \quad \Delta T = 0$ or $T_2 = T_1$
[$\because$ Internal energy of an ideal gas is a function of temperature.]
Applying ideal gas equation, $PV = nRT$
where n, R and T are constant.
then $P_1V_1 = P_2V_2$
Equation, PV^{γ} = constant, is applicable only for ideal gas in reversible adiabatic process.
Hence, $P_2V_2^{\gamma} = P_1V_1^{\gamma}$ equation is not applicable.

5. **(a, b, d) :** (a) Density of ice is less than water due to cage-like structure, in which each water molecule is surrounded by four other water molecules tetrahedrally through H-bonding. Hence, ice floats in water.

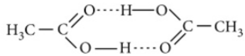
(b) $\underset{1^\circ \text{ amine}}{R-NH_2} + H-OH \rightleftharpoons \underset{(I)}{R-\overset{+}{N}H_3} + OH^-$

$\underset{3^\circ \text{ amine}}{R_3-N} + H-OH \rightleftharpoons \underset{(II)}{R_3-\overset{+}{N}H} + OH^-$

The cation (I) is more stabilised through hydrogen bonding than cation (II). So, $R-NH_2$ is stronger base than R_3N in aqueous solution.

(c) HCOOH is stronger acid than CH_3COOH due to inductive effect and not due to hydrogen bonding.

(d) Acetic acid dimerises in benzene through intermolecular hydrogen bonding.



6. **(a, b) :** Salt bridge keeps the solutions in two half-cells electrically neutral. It prevents transference or diffusion of the ions from one half-cell to the other.

7. **(b, c, d) :** (a) $CuFeS_2 + Cu_2S \xrightarrow{\Delta}$ No reaction

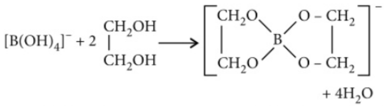
(b) $2CuO \xrightarrow{\Delta} Cu_2O + 1/2\ O_2$

(c) $2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$

(d) $CuSO_4 \xrightarrow{\Delta} CuO + SO_2 + 1/2\ O_2$

Both CuO and $CuSO_4$ upon heating produces Cu_2O and CuO respectively and further Cu_2O and CuO on heating with Cu_2S gives Cu.

8. **(b, d) :** (b) H_3BO_3 behaves as a weak monobasic acid *i.e.*, Lewis acid. It accepts a pair of electrons from OH^- ion.
$H-OH + B(OH)_3 \longrightarrow [B(OH)_4]^- + H^+$
(d) On adding ethylene glycol, its acidity increases.



H_3BO_3 does not undergo self-ionization and planar BO_3^{3-} units are joined by unsymmetrical hydrogen bonds to give a layered structure.

9. **(a, b, d) :** The balanced chemical equation is

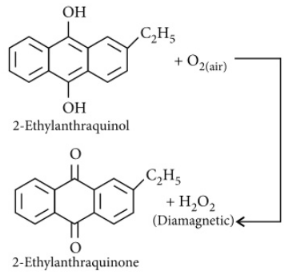
$$6I^- + ClO_3^- + 6H_2\overset{+6}{S}O_4 \longrightarrow Cl^- + 6H\overset{+6}{S}O_4^- + 3\overset{0}{I_2} + 3H_2O$$

oxidized (increase in O.N.)

10. **(a, b, c) :** (a) $Na + \underset{\text{(excess)}}{(x+y)NH_3} \longrightarrow [Na(NH_3)_x]^+ + \underset{\substack{\text{solvated } e^- \\ \text{(Paramagnetic)}}}{e^-(NH_3)_y}$

(b) $\underset{\text{(excess)}}{K + O_2} \longrightarrow \underset{\substack{\text{Potassium superoxide} \\ \text{(Paramagnetic)}}}{KO_2}$

(c) $3Cu + 8HNO_{3\,(dil.)} \longrightarrow 3Cu(NO_3)_2 + \underset{\text{(Paramagnetic)}}{2NO} + 4H_2O$

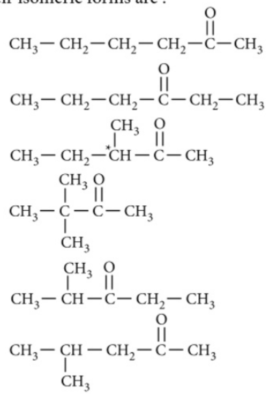
(d) 

11. (5) : General formula of ketone; $C_nH_{2n}O$

$12n + 2n + 16 = 100 \Rightarrow n = 6$

Hence, the ketone is $C_6H_{12}O$.

Their isomeric forms are :



Only structure (3) will not give racemic mixture on reaction with $NaBH_4$.

12. (4) : XeF_4 – Square planar

SF_4 – See-saw, SiF_4 – Tetrahedral

BF_4^- – Tetrahedral

BrF_4^- – Square planar

$[Cu(NH_3)_4]^{2+}$ – Square planar

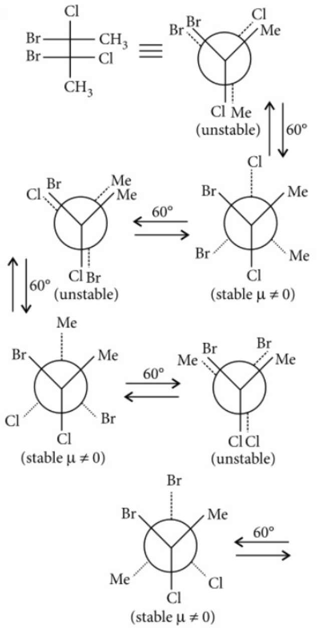
$[FeCl_4]^{2-}$ – Tetrahedral

$[CoCl_4]^{2-}$ – Tetrahedral

$[PtCl_4]^{2-}$ – Square planar

13. (7) : The black coloured sulphides are PbS, CuS, HgS, Ag_2S, NiS, CoS and Bi_2S_3. MnS is buff coloured while SnS_2 is yellow in colour.

14. (3) :



15. (7) : $6KI + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$

$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

$H_2O_2 + 2KI \longrightarrow I_2 + 2KOH$

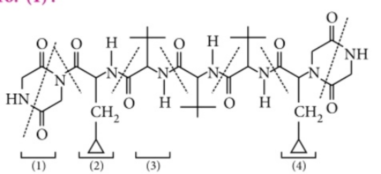
$Cl_2 + 2KI \longrightarrow 2KCl + I_2$

$O_3 + 2KI + H_2O \longrightarrow 2KOH + I_2 + O_2$

$2FeCl_3 + 2KI \longrightarrow 2FeCl_2 + 2KCl + I_2$

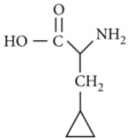
$4HNO_3 + 2KI \longrightarrow 2KNO_3 + 2NO_2 + I_2 + 2H_2O$

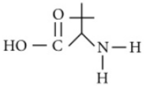
16. (1) :

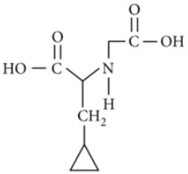


On acidic hydrolysis, 4 distinct amino acids were produced out of which only glycine is naturally occurring amino acid.

1. $H_2N-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$
Glycine (natural amino acid)

2. 

3. 

4. 

17. (6) : $n = 4, l = 0, 1, 2, 3$
$|m_l| = 1$ (only in p, d and f-orbitals)
2 electrons on each orbital have $m_s = -1/2$
Hence, total no. of electrons is 6.

18. (4) : Boltzmann constant, $k = \dfrac{R}{N_A}$
or, $R = k \times N_A$
$= 1.380 \times 10^{-23} \times 6.023 \times 10^{23}$
$= 8.31174 \text{ J K}^{-1} \text{ mol}^{-1} \approx 8.312$
Hence, no. of significant figure is 4.

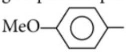
19. (8) : Mass of 1 L solvent $= 0.4 \text{ g mL}^{-1} \times 10^3 \text{ mL}$
$= 400 \text{ g} = 0.4 \text{ kg}$

So, molality $(m) = \dfrac{\text{Moles of solute}}{\text{Mass of solvent (kg)}} = \dfrac{3.2}{0.4}$
$= 8 \text{ m}$

20. (2) : $\underset{(1-\alpha)}{MX_2} \rightleftharpoons \underset{\alpha}{M^{2+}} + \underset{2\alpha}{2X^-}$
$i = 1 - \alpha + \alpha + 2\alpha$
$i = 1 + 2\alpha$ $\quad (\because \alpha = 0.5)$
$i = 1 + 2 \times 0.5 = 2$

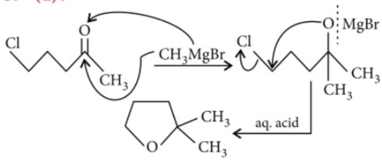
PAPER-II

1. (c) : Rate of S_N1 reaction is proportional to the stability of carbocation. When two phenyl groups are replaced by two

 groups, the carbocation formed will be more stable. Hence, the reaction is fastest.

2. (b) : More the branching, lesser will be the surface area and lesser will be the boiling point as van der Waals forces decrease.
Hence, the correct order of their boiling point is III > II > I.

3. (d) :



(Major product)

4. (a) : $\overset{+7}{K}IO_4 + \underset{\text{(Reducing agent)}}{H_2O_2} \longrightarrow \overset{+5}{K}IO_3 + H_2O + O_2$ (Decrease in O.N.)

$\overset{-1}{N}H_2OH + \underset{\text{(Oxidising agent)}}{3H_2O_2} \longrightarrow H\overset{+5}{N}O_3 + 4H_2O$ (Increase in O.N.)

5. (a) : $\underset{\text{(White)}}{P_4} + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

6. (c) :

$$XeF_6 + 3H_2O \xrightarrow[\text{hydrolysis}]{\text{Complete}} \underset{\text{'P'}}{XeO_3} + 6HF$$
$$\underset{\text{'P'}}{XeO_3} \xrightarrow{OH^-/H_2O} \underset{\text{'Q'}}{HXeO_4^-}$$
$$\underset{\text{'Q'}}{HXeO_4^-} \xrightarrow[\text{in } OH^-/H_2O]{\text{Slow disproportionation}} XeO_6^{4-} + Xe_{(g)} + H_2O + O_{2(g)}$$

7. (d) : In dye test, phenolic –OH is converted into –O⁻ ion, which activates the ring for further reaction. This is possible only in alkaline solution of β-naphthol. It dissolves poorly in aq. acidic solution.

8. (b) : $M \longrightarrow N$
$r = k[M]^x$ ...(i)
$8r = k[2M]^x$ ...(ii)
On dividing eqn. (ii) by (i), we get
or $8 = (2)^x \Rightarrow (2)^3 = (2)^x \Rightarrow x = 3$

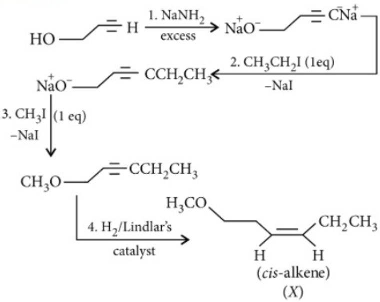
9. (b) : $H_2O_{(l)} \xrightarrow[\text{Boiling}]{\Delta} H_2O_{(g)}$
For this, $\Delta S_{\text{total}} = 0$
$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$
$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$
Hence, $\Delta S_{\text{system}} > 0$; $\Delta S_{\text{surroundings}} < 0$

10. (c) : If $2s$-$2p$ mixing is not operative, then molecular orbitals may be arranged in order of energy as follows :

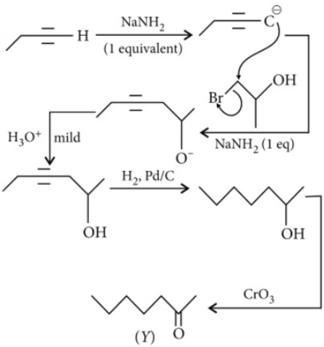
$\sigma 1s, \sigma^*1s, \sigma 2s, \sigma^*2s, \sigma 2p_z, \pi 2p_x = \pi 2p_y,$
$\pi^*2p_x = \pi^*2p_y, \sigma^*2p_z$

Applying this configuration, Be_2, B_2 and N_2 will be diamagnetic , but C_2 will be paramagnetic.

11. (a) :



12. (c) :



X and *Y* are functional isomers of each other and *Y* gives iodoform test.

13. (b):

$$\underset{\text{Tetrahedral, } sp^3\text{-hybridization}}{[NiCl_4]^{2-}} \xleftarrow[\text{excess}]{HCl\,(Q)} \underset{(M1)}{Ni^{2+}} \xrightarrow[\text{excess}]{KCN\,(R)} \underset{\text{Square planar, } dsp^2\text{-hybridization}}{[Ni(CN)_4]^{2-}}$$

14. (d):

$$\underset{\text{Tetrahedral}}{[ZnCl_4]^{2-}} \xleftarrow[\text{excess}]{HCl(Q)} \underset{(M2)}{Zn^{2+}} \xrightarrow[\text{excess}]{KCN(R)} \underset{\text{Tetrahedral}}{[Zn(CN)_4]^{2-}}$$

$$Zn^{2+} \xrightarrow{KOH(S)} \underset{\text{White ppt.}}{Zn(OH)_2} \xrightarrow[\text{excess}]{KOH(S)} \underset{\text{Soluble}}{[Zn(OH)_4]^{2-}}$$

15. (c) : According to Graham's law,

$$r \propto \frac{1}{\sqrt{M}}$$

As all conditions are identical for *X* and *Y*,

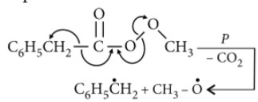
$$\frac{r_X}{r_Y} = \sqrt{\frac{M_Y}{M_X}} \Rightarrow \frac{d}{24-d} = \sqrt{\frac{40}{10}} = 2$$

$$d = 48 - 2d \Rightarrow 3d = 48$$

$$d = 16 \text{ cm}$$

16. (d): As the collision frequency increases, molecular speed decreases.

17. (a) : 1.



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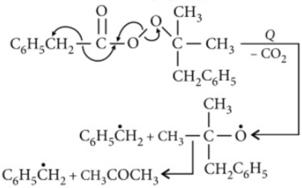

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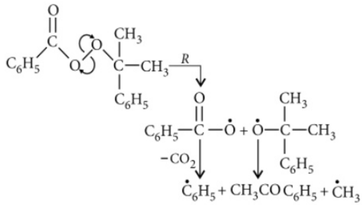
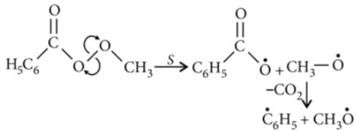
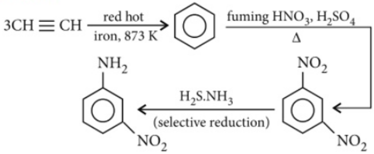
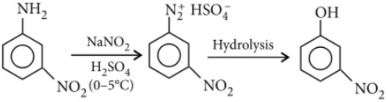


2.



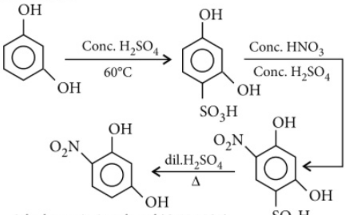
18. (c) : P : Scheme III





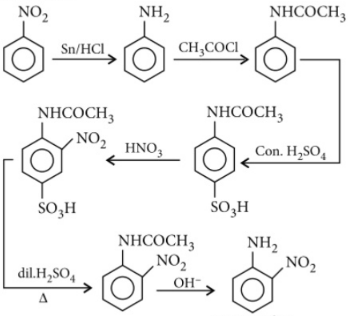
m-nitrophenol ($C_6H_5NO_3$)

Q : Scheme IV



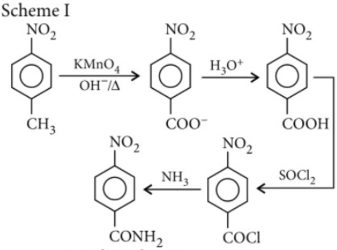
3-hydroxy-6-nitrophenol ($C_6H_5NO_4$)

R : Scheme II



o-nitroaniline
($C_6H_6N_2O_2$)

S : Scheme I



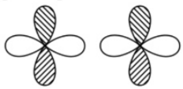
p-amidonitrobenzene
($C_7H_6N_2O_3$)

19. (b) : P : Cr^{3+} has $3d^3$ configuration, with 3 unpaired electrons. Hence, it shows paramagnetic behaviour. Complex of the type Ma_4b_2 shows *cis-trans* isomerism.

Q : Ti^{3+} has $3d^1$ configuration, hence shows paramagnetic behaviour. Complex gives Cl^- and NO_3^- ions in solution hence, shows ionisation isomerism.

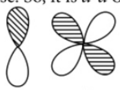
R : Pt^{2+} has $3d^8$ configuration but ligands are strong field ligands hence, it forms square planar complex. Thus, all electrons are paired and it also exhibits ionisation iosmerism.

S : Co^{3+} has $3d^6$ configuration. But, ligands present are strong enough to cause electron pairing, hence, it shows diamagnetic behaviour and exhibits *cis-trans* isomerism as it is Ma_4b_2 type complex.

20. (c) : P :  → Both the

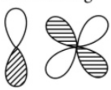
d d

d-orbitals show axial overlapping in same phase. So, it is d-d σ bonding.

Q :  → Both p-and d-orbitals

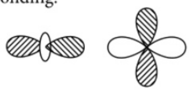
p d

show lateral overlapping in same phase. So, it is p-d π bonding.

R :  → Both p and d-orbitals

p d

overlap in opposite phase, so, it is p-d π antibonding.

S :  → Both the

d d

d-orbitals show axial overlapping in opposite phase. So, it is d-d σ antibonding.

EXAMINER'S MIND NCERT CLASS XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced) / AIPMT / AIIMS/other PMTs have drawn their papers heavily from NCERT books.

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES | CHEMICAL BONDING AND MOLECULAR STRUCTURE

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. Generally, the first ionization energy increases along a period but there are some exceptions. One which is not an exception is
   (a) N and O (b) Na and Mg
   (c) Mg and Al (d) Be and B

2. Hydrogen bonds are formed in many compounds *e.g.*, H_2O, HF, NH_3. The boiling point of such compounds depends to a large extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points of above compounds is
   (a) $HF > H_2O > NH_3$ (b) $H_2O > HF > NH_3$
   (c) $NH_3 > HF > H_2O$ (d) $NH_3 > H_2O > HF$

3. In a periodic table, the basic character of oxides
   (a) increases from left to right and decreases from top to bottom
   (b) decreases from right to left and increases from top to bottom
   (c) decreases from left to right and increases from top to bottom
   (d) decreases from left to right and increases from bottom to top.

4. The bond length between hybridised carbon atom and other carbon atom is minimum in
   (a) propene (b) propyne
   (c) propane (d) butane.

5. Which of the following is correct order of ionic size?
   (a) $Ca^{2+} > Cl^- > K^+ > S^{2-}$
   (b) $Ca^{2+} > K^+ > Cl^- > S^{2-}$
   (c) $Cl^- > K^+ > Ca^{2+} > S^{2-}$
   (d) $S^{2-} > Cl^- > K^+ > Ca^{2+}$

6. Which one of the following conversions involve change in both hybridisation and shape?
   (a) $CH_4 \rightarrow C_2H_6$ (b) $NH_3 \rightarrow NH_4^+$
   (c) $BF_3 \rightarrow BF_4^-$ (d) $H_2O \rightarrow H_3O^+$

7. The correct order of the increasing ionic character is
   (a) $BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2$
   (b) $BeCl_2 < BaCl_2 < MgCl_2 < CaCl_2$
   (c) $BeCl_2 < MgCl_2 < BaCl_2 < CaCl_2$
   (d) $BeCl_2 < CaCl_2 < MgCl_2 < BaCl_2$

8. The pair having similar geometry is
   (a) BF_3, NH_3 (b) CO_2, SO_2
   (c) H_2O, C_2H_2 (d) NH_3, PH_3

9. An element has atomic number 79. Predict the group and period in which the element is placed.
   (a) 2^{nd} group, 7^{th} period
   (b) 11^{th} group, 6^{th} period
   (c) 13^{th} group, 6^{th} period
   (d) 12^{th} group, 6^{th} period

10. Two elements P and Q combine to form a compound. If P has 2 and Q has 6 electrons in their outermost shell, what will be the formula of the compound formed?
(a) PQ (b) P_2Q
(c) P_2Q_3 (d) PQ_2

11. Which of the following is a strong reducing agent?
(a) Cr (b) Cl
(c) Na (d) Ca

12. Which of the following statements is not true?
(a) Ionic bonds are non-directional while covalent bonds are directional.
(b) Formation of π-bond shortens the distance between the two concerned atoms.
(c) Ionic bond is possible between similar and dissimilar atoms.
(d) Linear overlapping of atomic p-orbitals leads to a sigma bond.

13. In which of the following, the order is not in accordance with the property mentioned?
(a) Li < Na < K < Rb – Atomic radius
(b) F > N > O > C – Ionisation enthalpy
(c) Si < P < S < Cl – Electronegativity
(d) F < Cl < Br < I – Electronegativity

14. In NO_3^- ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are
(a) 2, 2 (b) 3, 1
(c) 1, 3 (d) 4, 0

15. Which of the following relation is correct with respect to first (I) and second (II) ionization potentials of sodium and magnesium?
(a) $I_{Mg} = II_{Na}$ (b) $II_{Mg} > II_{Na}$
(c) $I_{Na} > I_{Mg}$ (d) $II_{Na} > II_{Mg}$

16. An example of polar covalent compound is
(a) HCl (b) CH_4
(c) CCl_4 (d) NaCl

17. Which group of elements shows lowest ionisation enthalpy?
(a) Alkali metals
(b) Alkaline earth metals
(c) Halogens
(d) Noble gases

18. What is the correct mode of hybridisation of the central atom in the following compounds?

	NO_2^+	SF_4	PF_6^-
(a)	sp^2	sp^3	d^2sp^3
(b)	sp^3	sp^3d^2	sp^3d^2
(c)	sp^2	sp^3d	sp^3d^2
(d)	sp	sp^2	sp^3

19. Few elements are matched with their successive ionisation energies. Identify the elements.

Element	IE_1 (kJ/mol)	IE_2 (kJ/mol)
X	2372	5251
Y	520	7297
Z	900	1758

	X	Y	Z
(a)	A noble gas	Alkali metal	Alkaline earth metal
(b)	Alkali metal	A noble gas	Alkaline earth metal
(c)	Alkaline earth metal	Alkali metal	A noble gas
(d)	Alkali metal	Alkaline earth metal	A noble gas

20. Four diatomic species are listed below. Identify the correct order in which the bond order is increasing in them.
(a) $NO < O_2^- < C_2^{2-} < He_2^+$
(b) $O_2^- < NO < C_2^{2-} < He_2^+$
(c) $C_2^{2-} < He_2^+ < O_2^- < NO$
(d) $He_2^+ < O_2^- < NO < C_2^{2-}$

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. In which of the following sets of atomic numbers all elements are in the same group?
(a) 8, 16, 24 (b) 3, 11, 37
(c) 12, 38, 56 (d) 10, 18, 54

22. Which of the following are diamagnetic?
(a) C_2 (b) He_2
(c) Li_2 (d) N_2

23. Which of the following statements regarding the variation of atomic radii in the periodic table is not true?
   (a) In a group, there is continuous increase in size with increase in atomic number.
   (b) In 4*f*-series, there is a continuous decrease in size with increase in atomic number.
   (c) The size of inert gases is larger than halogens.
   (d) In 3^{rd} period, the size of atoms increases with increase in atomic number.

24. Mark out the incorrect match of shape.
   (a) $XeOF_2$ — Trigonal planar
   (b) ICl_4^- — Square planar
   (c) $[SbF_5]^{2-}$ — Square pyramidal
   (d) NH_2^- — Pyramidal

25. The isoelectronic pairs are
   (a) Na^+, Mg^{2+} (b) Mg^{2+}, F^-
   (c) NO^+, N_2 (d) NO^+, CO

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

The atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape.

26. Which of the following has sp^2-hybridisation?
   (a) $BeCl_2$ (b) C_2H_2
   (c) C_2H_6 (d) C_2H_4

27. One *s* and three *p*-orbitals on hybridisation give
   (a) four orbitals with tetrahedral orientation
   (b) three orbitals with trigonal orientation
   (c) two orbitals with linear orientation
   (d) two orbitals with perpendicular orientation.

28. Which of the following statements is true about hybridisation?
   (a) The hybridised orbitals have different energies for each orbital.
   (b) The number of hybrid orbitals is equal to the number of atomic orbitals that are hybridised.
   (c) Hybrid orbitals form multiple bonds.
   (d) The orbitals with different energies undergo hybridisation.

Paragraph for Questions 29 to 31

Across the period, successive electrons are added to orbitals in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. As we go down a group, the outermost electron being increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels.

29. The ionization energy of elements in a period increases as we proceed from left to right because
   (a) the number of electrons increases successively
   (b) the number of neutrons increases successively
   (c) the number of protons increases successively
   (d) electrons being filled in orbitals with same principal quantum number experience more nuclear charge.

30. The order of screening effect of electrons of *s*, *p*, *d* and *f* orbitals of a given shell of an atom on its outer shell electrons is
   (a) $s > p > d > f$ (b) $f > d > p > s$
   (c) $p < d < s > f$ (d) $f > p > s > d$

31. Which of the following has the highest electron affinity?
   (a) F^- (b) O^-
   (c) O (d) Na

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY one is correct.

32. Match the List I with List II and select the correct answer using the code given below the lists.

	List I		List II
P.	sp^2	1.	ICl_4^-
Q.	dsp^2	2.	$Fe(CO)_5$
R.	sp^3d	3.	$SnCl_2$
S.	sp^3d^2	4.	$[Ni(CN)_4]^{2-}$

	P	Q	R	S
(a)	1	2	3	4
(b)	3	2	1	4
(c)	3	4	2	1
(d)	4	3	1	2

33. Match the List I with List II and select the correct answer using the code given below the lists.

	List I Class of elements		List II Elements
P.	Alkaline earth metals	1.	Rn
Q.	Chalcogens	2.	Te
R.	Halogens	3.	Sr
S.	Noble gases	4.	At

	P	Q	R	S
(a)	3	2	4	1
(b)	4	2	1	3
(c)	4	3	2	1
(d)	1	2	3	4

34. Match the List I with List II and select the correct answer using the code given below the lists.

	List I		List II
P.	SiF_4	1.	Pyramidal molecule
Q.	NH_3	2.	Tetrahedral molecule
R.	BeF_2	3.	Zero dipole moment
S.	BF_3	4.	Linear molecule.

	P	Q	R	S
(a)	3	2	1	4
(b)	1	4	3	2
(c)	4	3	2	1
(d)	2	1	4	3

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

35. **Assertion :** For the element O or F, the electron gain enthalpy is less negative than that of the succeeding element.
Reason : Electron gain enthalpy becomes less negative as we go down a group.

36. **Assertion:** PF_5, SF_6 and H_2SO_4 are the examples of expanded octet molecules.
Reason : Octet rule is not applicable to the second period elements of the periodic table.

37. **Assertion :** Metallic character is highest at the extremely left side of the periodic table.
Reason : Ionization enthalpy increases across a period.

38. **Assertion :** Sodium chloride (NaCl) is a stable ionic solid.
Reason : NaCl has high lattice enthalpy.

39. **Assertion :** The atomic size generally increases across a period and decreases down the group.
Reason : Atomic size depends upon valence shell electronic configuration.

40. **Assertion :** O_2 molecule is diamagnetic while C_2 molecule is paramagnetic in nature.
Reason : Bond order of O_2 molecule is 1.5 and that of C_2 molecule is 2.5.

SECTION - VI

Integer Value Correct Type

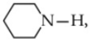
This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. The number of isoelectronic species in the following are

$$CN^-, N_2, O_2^{2-}, NO^+, C_2^{2-}, CO, O_2^-$$

42. The no. of orbitals involved in the hybridization in NO_2^+ ion is

43. The element with maximum electronegativity belongs to period

44. In piperidine, , N atom has sp^x hybridisation. The value of x is

45. Number of valence shell electrons in Cl^- is

46. A planar molecule has AB_x structure with six bond pairs of electrons around A and one lone pair. The value of x is

47. Electronegativity value of chlorine on Mulliken's scale if $IP = 13.0$ eV and $EA = 4.0$ eV is

48. Number of molecules that do not follow octet rule among the following is

$$CO, PCl_5, PCl_3, AlCl_3, SF_6, BF_3, NH_3$$

49. The element with atomic number 26 will be found in group

50. The formal charge on the central oxygen atom in O_3 molecule is

SOLUTIONS

1. **(b) :** Na and Mg is not an exception. The first ionization enthalpy of elements of group 2 are greater than those of group 1 due to their smaller size and higher nuclear charge.

2. **(b) :** Strength of hydrogen bonding depends on the size and electronegativity of the atom. Smaller the size of the atom, greater is the electronegativity and hence stronger is the H-bonding. Thus, the order of strength of H-bonding is H...F > H...O > H...N. But each HF molecule is linked only to two other HF molecules while each H_2O molecule is linked to four other H_2O molecules through H-bonding.
Hence, the decreasing order of boiling points is $H_2O > HF > NH_3$.

3. **(c) :** As the electronegativity of element increases, acidic character of oxides increases. So, in a group, basic nature increases on moving down and decreases along a period.

4. **(b) :** Higher the bond order, smaller is the bond length, since propyne has a triple bond, therefore it has minimum bond length. The $C-C$ bond length is 1.54 Å, $C=C$ bond length is 1.34 Å and $C\equiv C$ bond length is 1.20 Å.

5. **(d) :** $S^{2-} > Cl^- > K^+ > Ca^{2+}$
An anion is always larger than a cation and for isoelectronic species, higher the nuclear charge smaller is the size.

6. **(c) :**

Compound	Hybridisation	Shape
CH_4	sp^3	Tetrahedral
C_2H_6	sp^3	Tetrahedral
NH_3	sp^3	Trigonal pyramidal
NH_4^+	sp^3	Tetrahedral
BF_3	sp^2	Trigonal planar
BF_4^-	sp^3	Tetrahedral
H_2O	sp^3	Angular
H_3O^+	sp^3	Tetrahedral

7. **(a) :** Ionic character decreases with decrease in size of cation and increase in size of anion. As anion (Cl^-) is same in given case, the correct order of increasing ionic character is

$$BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2.$$

8. **(d) :** Both NH_3 and PH_3 have a pyramidal structure.

9. **(b) :** $Z = 79$, $[Xe]4f^{14}\,5d^{10}\,6s^1$ $(n = 6)$
As $n = 6$, the element belongs to 6^{th} period.
Group = $ns + (n - 1)d$, $1 + 10 = 11$

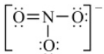
10. **(a) :** Valence electrons in P is 2.
Valence electrons in Q is 6.
$P - 2e^- \rightarrow P^{2+}$
$Q + 2e^- \rightarrow Q^{2-}$
Since both show a valency of 2, the formula for the compound will be PQ.

11. **(c) :** Ionization energy for Na is very low as compared to other metals. So it acts as a good reducing agent.

12. **(c) :** Ionic bond cannot be formed between two similar atoms.

13. **(d) :** Electronegativity decreases down the group as the size of the atom increases.

14. **(d) :** The Lewis representation of NO_3^- ion is



Thus, N atom has 4 bond pairs only.

15. **(d) :** Electronic configuration of Na is

$$1s^2\,2s^2\,2p^6\,3s^1$$

Electronic configuration of Na^+ is $1s^2\,2s^2\,2p^6$

Electronic configuration of Mg is $1s^2\,2s^2\,2p^6\,3s^2$

Electronic configuration of Mg^+ is $1s^2\,2s^2\,2p^6\,3s^1$

Electronic configuration of Na^+ corresponds to noble gas configuration. So, more energy is required to remove second electron from Na.

$\therefore\ \ II_{Na} > II_{Mg}$

16. **(a) :** In HCl, electrons are shared unequally due to difference in electronegativity of H and Cl.

17. **(a) :** Ionization energy increases along a period. Alkali metals can most easily loose ns^1 electron to attain noble gas configuration.

18. **(c)**

19. **(a) :** X has highest IE_1 and IE_2 hence, it is a noble gas.

Y has low IE_1, but very high IE_2 hence, it is an alkali metal.

Z has low IE_1 than IE_2 and IE_2 is even lower than IE_2 of alkali metal hence, it is an alkaline earth metal.

20. **(d) :**

Diatomic species	Bond order
NO	2.5
O_2^-	1.5
C_2^{2-}	3.0
He_2^+	0.5

Thus increasing order : $He_2^+ < O_2^- < NO < C_2^{2-}$

21. **(b, c, d) :** $3 + 8 = 11 + 8 = 19 + 18 = 37$

$12 + 8 = 20 + 18 = 38 + 18 = 56$

$10 + 8 = 18 + 18 = 36 + 18 = 54$

22. **(a, b, c, d)**

23. **(d) :** Size of atoms decreases with increase in atomic number in a period.

24. **(a, d) :** $XeOF_2 : sp^3d$, T-shaped

$NH_2^- : sp^3$, V-shaped

25. **(a, b, c, d) :** All are isoelectronic pairs.

Na^+ and Mg^{2+} have 10 electrons.

Mg^{2+} and F^- have 10 electrons.

NO^+ and N_2 have 14 electrons.

NO^+ and CO have 14 electrons.

26. **(d) :** $BeCl_2$ and C_2H_2 have sp-hybridisation and C_2H_6 has sp^3-hybridisation.

27. **(a) :** Four sp^3 hybrid orbitals are formed when one s and three p-orbitals hybridise.

28. **(b) :** The number of orbitals which hybridise remains same after the hybridisation.

29. **(d) :** When we go from left to right in a period, the nuclear charge increases by one unit at each element and added electrons enter into the same shell. Since, the electrons in the same shell do not shield each other from the nucleus effectively, hence the atomic size decreases, due to increase in effective nuclear charge and ionisation energy increases in going from left to right in a period.

30. **(a) :** For the same shell, screening effect decreases in the order : $s > p > d > f$.

31. **(c) :** Electron affinity is the amount of energy released. Energy is released when electron is added to O but energy is required to add electron to F^-, O^- and Na^+.

32. **(c)**

33. **(a)**

34. **(d)**

35. **(b) :** Generally, electron gain enthalpy becomes less negative (decreases) as we go down the group because size of the atom increases and the added electron will be farther from the nucleus.

But in case of O or F, the added electron goes to the smaller quantum level *i.e.*, $n = 2$ and suffers significant repulsion from other electrons present in this level.

36. **(c) :** In PF_5, SF_6 and H_2SO_4, the central atom has more than eight valence electrons hence they exhibit expanded octet. This is possible due to availability of 3*d* orbitals.
Elements in and beyond the third period of the periodic table do not follow octet rule thus it applies mainly to the second period elements of the periodic table.

37. **(a)** 38. **(a)**

39. **(d) :** Atomic size generally decreases across a period because within the period, the outer electrons are added in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus. Whereas, on going down the group atomic size increases regularly because the principal quantum number increases and the valence electrons are farther from the nucleus. Also, inner electrons shield the outer electrons from the pull of the nucleus.

40. **(d) :** $O_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-6) = 2$$

It contains two unpaired electrons hence it is paramagnetic in nature.

$C_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$

$$\text{Bond order} = \frac{1}{2}(8-4) = 2$$

All electrons are paired hence it is diamagnetic in nature.

41. **(5) :** $CN^- = 6 + 7 + 1 = 14e^-$
$N_2 = 7 + 7 = 14e^-$
$O_2^{2-} = 8 + 8 + 2 = 18e^-$
$C_2^{2-} = 6 + 6 + 2 = 14e^-$
$O_2^- = 8 + 8 + 1 = 17e^-$
$NO^+ = 7 + 8 - 1 = 14e^-$
$CO = 6 + 8 = 14e^-$

42. **(2) :** Using the formula, $H = \frac{1}{2}[V + M - C + A]$

H = number of orbitals involved in hybridization
V = valence electrons of central atom
M = no. of monovalent atoms linked with central atom
C = charge on cation
A = charge on anion
In NO_2^+ : $V = 5$; $M = 0$; $C = 1$; $A = 0$

$$H = \frac{1}{2}(5 + 0 - 1 + 0) = 2$$

43. **(2) :** The element is fluorine.

44. **(3) :** N on piperidine has 3 σ-bonds and one lone pair of electrons, hence, N is sp^3 hybridised, so, *x* is 3.

45. **(8) :** $Cl^- = 1s^2 2s^2 2p^6 \boxed{3s^2 3p^6}$

Number of valence electrons is 8.

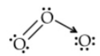
46. **(6) :** Six *B* are attached to *A i.e*, AB_6
Hence, value of *x* is 6.

47. **(3) :** $EN = \frac{IP + EA}{5.6} = \frac{13.0 + 4}{5.6} = 3.035 \approx 3$

48. **(4) :** BF_3, $AlCl_3$ are electron deficient molecules while in PCl_5 and SF_6 molecules, P and S possess more than 8 electrons in their valence shells.

49. **(8) :** Electronic configuration = [Ar] $3d^6 4s^2$
Group = 8^{th}

50. **(1) :** The Lewis dot structure of O_3 is



Formal charge on the central oxygen atom = [Valence electrons – Non-bonding electrons – 1/2 (Total number of bonding electrons)]

$$= 6 - 2 - \frac{1}{2} \times 6 = 1$$

Foundation Series

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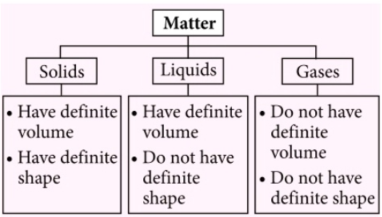
UNIT-1 Some Basic Concepts in Chemistry | States of Matter | Atomic Structure | Chemical Bonding and Molecular Structure

SOME BASIC CONCEPTS IN CHEMISTRY

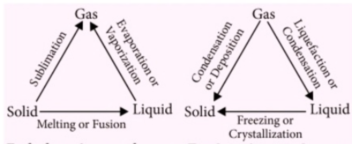
- Introduction
- Physical and Chemical Classification of Matter
- Units and Measurements
- Laws of Chemical Combination
- Dalton's Atomic Theory
- Atomic, Molecular Masses and Mole Concept

TIPS TO REMEMBER

- Chemistry deals with the composition, structure and properties of matter which can be described and understood in terms of basic constituents of matter *i.e.*, *atoms* and *molecules*.
- Anything which has mass and occupies space is called *matter*.
- **Physical Classification of Matter**

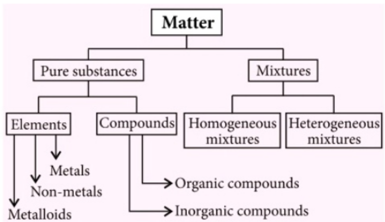


- The three states of matter can be interconverted by changing the conditions of temperature and pressure as follows :



Endothermic state changes **Exothermic state changes**

- **Chemical Classification of Matter**



Units and Measurements

- The units of mass, length and time are called *fundamental units* since they are independent units and cannot be derived from any other units. They are also called *basic units*.

- The units for other quantities which can be derived from fundamental units are called *derived units.*
- The units adopted by the General Conference of Weights and Measures is known as SI unit or systeme internationale.
- The SI system has seven basic units :

Physical quantity	Symbol for quantity	Name of unit	Symbol for unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Temperature	T	kelvin	K
Electric current	I	ampere	A
Luminous intensity	I_v	candela	cd
Amount of substance	n	mole	mol

- Accuracy is the agreement of a particular value to the true value of the result.
- Precision refers to the closeness of various measurements for the same quantity.
- Significant figures are those digits in a measured number that include all certain digits and one doubtful digit.
- Rules for determining the number of significant figures :
  - All non-zero digits are significant.
  - A zero becomes significant when it comes in between two non-zero numbers.
  - Zeros at the beginning of a number are not significant.
  - All zeros to the right of a number are significant.
- **Dimensional analysis :** The expression of any particular quantity in terms of fundamental quantity is known as *dimensional analysis.*
  - This can be done by method called *factor label method* or *unit factor method.*
  - This is done by using conversion factor (C.F.), which is a factor equal to one that converts a quantity in one unit to the same quantity in another unit. Some conversion factors are as follows :
    $1\ J = 10^7$ erg
    1 atm = 760 torr = 760 mm Hg

Laws of Chemical Combination

- **Law of conservation of mass :** It states that during any physical or chemical change, total mass of products is equal to the total mass of reactants.
  e.g., $\underset{12\ g}{C} + \underset{32\ g}{O_2} \longrightarrow \underset{44\ g}{CO_2}$
  Mass of CO_2 = Mass of C + Mass of O_2
- **Law of definite proportion :** It states that a compound always contains the same elements combined in the same definite proportion by weight. *e.g.*, Water (H_2O) obtained from any source always contains 2 g of hydrogen in combination with 16 g of oxygen.
- **Law of multiple proportion :** It states that when two or more elements combine to form two or more compounds, the different weights of one of the elements which combine with the fixed weight of the other, bear a simple whole number ratio to one another.
  e.g., The ratio between the weights of oxygen in different compounds which combine with the same weight of N (14 parts) is

$$\begin{array}{ccccc} 8 & : & 16 & : & 24 \\ 1 & : & 2 & : & 3 \\ N_2O & & NO & & N_2O_3 \end{array}$$

- **Law of reciprocal proportion :** It states that when two elements combine separately with a fixed mass of third element, then the ratio between their masses in which they combine will be either same or simple multiple of the ratio in which they combine with each other.
- **Gay Lussac's law of combining volumes :** It states that under similar conditions of temperature and pressure, whenever gases react together, the volumes of the reacting gases as well as products bear a simple whole number ratio.

Dalton's Atomic Theory

- Matter is made up of small indivisible particles called *atoms*.
- Atoms can neither be created nor destroyed.
- Atom is the smallest unit that takes part in chemical combination.
- Atoms of two or more elements combine in whole number ratio to form compound atoms (or molecules).
- Atoms of the same element have identical shape, size, mass and chemical properties.
- Atoms of different elements differ in their mass and chemical properties.

Atomic Mass

- Atomic mass of an element is defined as the average relative mass of an atom of an element as compared to the mass of an atom of carbon (^{12}C) taken as 12.
- **Calculation of atomic weight**
  - Atomic wt. × specific heat = 6.4 (approx.) **(Dulong and Petit's law for solids)**

    $$\therefore \text{ Approx. atomic weight} = \frac{6.4}{\text{sp. heat}}$$

    $$\text{Valency} = \frac{\text{Approx. At. wt.}}{\text{Eq. wt.}}$$

    Atomic weight = Eq. wt. × valency
  - Valency of the metal whose chloride is volatile $= \dfrac{2 \times \text{V.D. of metal chloride}}{\text{Eq. wt. of metal} + 35.5}$

Molecular Mass

- Molecular mass of a substance is the average relative mass of its molecule as compared to the mass of an atom of carbon (^{12}C) taken as 12.
- **Calculation of molecular mass**
  - Molecular mass = 2 × Vapour density
  - Molecular mass = Mass of 22.4 L of vapour at STP
  - Rates of diffusion, $\dfrac{r_1}{r_2} = \sqrt{\dfrac{M_2}{M_1}}$

Mole Concept

- 1 Mole of atoms
  = Gram atomic mass (or 1 g atom)
  = 6.022×10^{23} atoms
- 1 Mole of molecules = Gram molecular mass (or 1 g molecule)
  = 6.022×10^{23} molecules = 22.4 L at STP

Calculation of Equivalent Weight

- $$\text{Eq. wt. of metal} = \frac{\text{Wt. of metal}}{\text{Wt. of } H_2 \text{ displaced}} \times 1.008$$

  $$= \frac{\text{Wt. of metal}}{\text{Vol. of } H_2 \text{ in mL displaced at STP}} \times 11200$$
- $$\text{Eq. wt. of metal} = \frac{\text{Wt. of metal}}{\text{Wt. of oxygen combined}} \times 8$$

  $$= \frac{\text{Wt. of metal}}{\text{Wt. of } O_2 \text{ displaced/combined in mL at STP}} \times 5600$$
- Eq. wt. of metal

  $$= \frac{\text{Wt. of metal}}{\text{Wt. of chlorine combined}} \times 35.5$$

  $$= \frac{\text{Wt. of metal}}{\text{Vol. of } Cl_2 \text{ combined in mL at STP}} \times 11200$$
- $$\frac{\text{Wt. of metal added to a salt solution}}{\text{Wt. of metal displaced}} = \frac{\text{Eq. wt. of metal added}}{\text{Eq. wt. of metal displaced}}$$
- $$\frac{\text{Wt. of salt } AB \text{ added to salt } CD \text{ (in solution)}}{\text{Wt. of ppt. } AD \text{ formed}} = \frac{\text{Eq. wt. of radical } A + \text{Eq. wt. of radical } B}{\text{Eq. wt. of radical } A + \text{Eq. wt. of radical } D}$$
- Eq. wt. = wt. deposited by 1 Faraday (96500 coulombs)
- On passing the same quantity of electricity through two different electrolytic solutions,

  $$\frac{\text{Wt. of } X \text{ deposited}}{\text{Wt. of } Y \text{ deposited}} = \frac{\text{Eq. wt. of } X}{\text{Eq. wt. of } Y}$$
- Eq. wt. of an acid = Wt. of the acid neutralized by 1000 cc of 1 N base solution

  Eq. wt. of a base = Wt. of the base neutralized by 1000 cc of 1 N acid solution

- For an organic acid ($RCOOH$)

$$\frac{\text{Eq. wt. of silver salt } (RCOOAg)}{\text{Eq. wt. of silver } (108)} = \frac{\text{Wt. of silver salt}}{\text{Wt. of silver}}$$

Eq. wt. of acid ($RCOOH$)

$$= \text{Eq. wt. of } RCOOAg - 107$$

- $\text{Eq. wt. of an acid} = \dfrac{\text{Mol. wt. of the acid}}{\text{Basicity}}$

$\text{Eq. wt. of a base} = \dfrac{\text{Mol. wt. of the base}}{\text{Acidity}}$

Eq. wt. of a salt

$$= \frac{\text{Mol. wt. of the salt}}{\text{Total positive valency of the metal atoms}}$$

- Eq. wt. of oxidizing/reducing agent

$$= \frac{\text{Mol. wt. of the substance}}{\text{No. of electrons gained/lost by one molecule}}$$

Determination of Chemical Formula

- Empirical formula gives the simple whole number ratio of the atoms of various elements present in one molecule of the compound.
- Molecular formula gives the actual number of atoms of various elements present in one molecule of the compound.
- Molecular formula = n (Empirical formula), where $n = 1, 2, 3, \ldots$

Concentration of a Solution

- $\text{Mass \% of } A = \dfrac{W_A}{W_A + W_B} \times 100$
- $\text{Volume \% of } A = \dfrac{V_A}{V_A + V_B} \times 100$
- Parts per million of A

$$= \frac{\text{Mass of component } A}{\text{Total mass of solution}} \times 10^6$$

- $\text{Molarity } (M) = \dfrac{\text{Moles of solute}}{\text{Volume of solution (mL)}} \times 1000$
- $\text{Molality } (m) = \dfrac{\text{Moles of solute}}{\text{Mass of solvent (g)}} \times 1000$
- $\text{Normality } (N) = \dfrac{\text{Gram equiv. of solute}}{\text{Volume of solution (mL)}} \times 1000$

$$= \text{Molarity} \times \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

Limiting Reagent

- The reactant which is completely consumed in the reaction and hence limits the amount of product formed is called *limiting reagent*.
- In case where there is a limiting reagent, the initial amount of the limiting reagent must be used to calculate the amount of product formed.

Key Points

For a reaction, $X + Y \rightarrow Z$

If $\dfrac{n_X \text{ (initial)}}{n_Y \text{ (initial)}} < S\left(\dfrac{X}{Y}\right)$, then X is limiting

If $\dfrac{n_X \text{ (initial)}}{n_Y \text{ (initial)}} > S\left(\dfrac{X}{Y}\right)$, then Y is limiting

where, n_X and n_Y are the moles of X and Y. S is the stoichiometric ratio of X and Y.

STATES OF MATTER

- Introduction
- Gaseous State
- Liquid State
- Solid State

TIPS TO REMEMBER

GASEOUS STATE

- Matter exists in three states - *solids*, *liquids* and *gases*. The fourth, *plasma state*, is the ionic state of atoms existing at very high temperatures found only in the interior of stars.
- The three states can be considered to arise as a result of competition between two opposing forces.
  - Forces of attraction holding the molecules together.
  - Disruptive forces due to thermal energy of the molecules.
- $\xrightarrow{\hspace{6em}}$ Forces of attraction

  (min) Gases (max) Liquids (max) Solids (min)

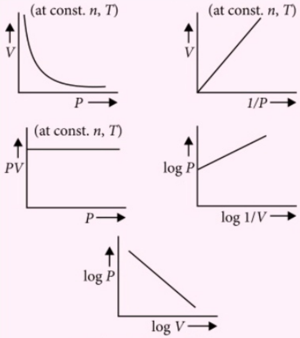
  $\xleftarrow{\hspace{6em}}$ Thermal energy
- **Measurable properties of gases :**
  - Mass (S.I. unit kg)
  - Volume (S.I. unit m^3)
  - Pressure (S.I. unit Pa)
  - Temperature (S.I. unit K)
- **Standard temperature and pressure or STP :** 0 °C or 273.15 K and 1 atm or 760 mm Hg or 101.325 kPa

Gas Laws

- **Boyle's law :** It states that at constant temperature, pressure of a fixed amount of gas varies inversely with the volume of the gas.

  i.e., at constant T and n, $P \propto \frac{1}{V}$

  or $PV = k = \text{constant}$ or $P_1V_1 = P_2V_2$



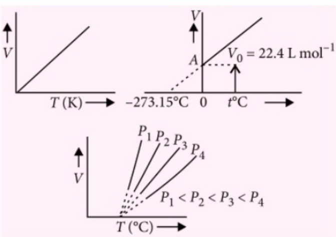
Isotherms for Boyle's law

- **Charles' law :** It states that at constant pressure, the volume of a given mass of a gas increases or decreases by 1/273 of its volume at 0 °C for each one degree rise or fall in temperature.
  i.e., if volume of a gas at 0 °C and t °C are V_0 and V_t then,

  $$V_t = V_0 + \frac{t}{273.15}V_0 = V_0\left[1 + \frac{t}{273.15}\right]$$

  - Charles' law can also be represented as

    $V \propto T$ at constant P. *i.e.*, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$



  - The theoretically possible temperature at which the volume of the gas becomes zero is called *absolute temperature* and corresponds to −273 °C.
  - When the temperature of a substance is lowered, the thermal energy reduces. Absolute zero (0 K) is the temperature reached when all possible thermal energy has been removed from a substance. A substance cannot be cooled any further after all thermal energy has been removed.
  - At absolute zero temperature, the total kinetic energy of the molecule becomes zero and hence molecular motion ceases.

- **Gay-Lussac's law :** It states that at constant volume, pressure of a fixed amount of a gas varies directly with temperature.
  i.e., $P \propto T \Rightarrow P/T = k = \text{constant}$

  or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

- **Avogadro' s law :** It states that at a given temperature and pressure, the volume of a gas is directly proportional to the amount of gas.
  i.e., at constant P and T,

  $V \propto n$ (n = amount of substance)

- All the gas laws can be combined to give the *combined gas law* or *gas equation* as follows :

  Boyle's law : $V \propto \frac{1}{P}$

  Charles' law : $V \propto T$

  Avogadro's law : $V \propto n$

  $\Rightarrow V \propto \frac{nT}{P}$ or $PV \propto nT$

  $\Rightarrow PV = nRT$; Ideal gas equation

  where R is the constant of proportionality and is known as *gas constant* or *universal gas constant*.

- **Values of R :**
  - 0.0821 L atm K^{-1} mol^{-1}
  - 8.314×10^7 ergs K^{-1} mol^{-1} (C.G.S. unit)
  - 8.314 J K^{-1} mol^{-1} (M.K.S. unit)
  - $1.987 \approx 2$ cal K^{-1} mol^{-1}

- **Graham's law of diffusion :** It states that under similar conditions of temperature and pressure, rates of diffusion of different gases are inversely proportional to the square root of their densities.

i.e., $\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}}=\sqrt{\frac{M_2}{M_1}}=\frac{V_1}{V_2}\times\frac{t_2}{t_1}$

(where t = time of diffusion)

Molecular weight = 2 × Vapour density

Also, $\frac{r_1}{r_2}=\frac{n_1}{n_2}\times\frac{t_2}{t_1}=\frac{D_1}{D_2}\times\frac{t_2}{t_1}=\frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$

(where D = distance travelled)

- *Effusion* is escape of a gas through a tiny hole.
- **Dalton's law of partial pressures :** It states that the total pressure exerted by a mixture of two or more non-reacting gases is equal to the sum of partial pressures of each component when present in the same container at same temperature.

  i.e., $P_{mix} = p_1 + p_2 + p_3 + ...$

  $= (n_1 + n_2 + n_3 + ...)\frac{RT}{V}$

Kinetic Theory of Gases

- The macroscopic behaviour of gases can be explained by a model containing three hypotheses.
  - Gas consists of particles in continuous, fast random motion, moving in straight lines until they collide.
  - The particles are infinitely small and (on the average) far from each other. (volume of the particles <<< volume of the gas).
  - The particles do not influence one another except during collisions. The collisions of the particles with each other and with the walls of the container are elastic, *i.e.*, the kinetic energy of the particles is maintained (there is no transformation of kinetic energy into heat or friction).
- The pressure of a gas exerted on the walls of the container is caused by the collision of the gas particles with the wall.
- Kinetic gas equation was proposed by Maxwell,

  $$PV=\frac{1}{3}mnu^2$$

  where, P = pressure of gas, V = volume of gas, m = mass of one molecule of gas, n = number of molecules of gas, u = root mean square velocity of molecules.

  Also, $PV=\frac{1}{3}Mu^2$ for 1 mole,

  M (mol. wt.) = mn

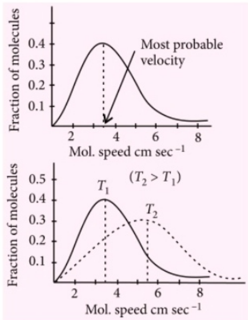
- Average kinetic energy, $KE=\frac{3}{2}kT$

  where k = Boltzmann constant = $\frac{R}{N_A}$
- Average speed, $u_{av}=\frac{u_1+u_2+u_3+...}{N}$

  or $u_{av}=\frac{N_1u_1+N_2u_2+N_3u_3+...}{N_1+N_2+N_3+...}=\sqrt{\frac{8RT}{\pi M}}$
- Root mean square speed,

  $$u_{r.m.s.}=\sqrt{\frac{u_1^2+u_2^2+u_3^2+...}{N}}=\sqrt{\frac{3RT}{M}}$$
- Most probable velocity is the speed possessed by maximum fraction of molecules of a gas.

  $$u_{mp}=\sqrt{\frac{2RT}{M}}$$



Real Gases and Deviation from Ideal Behaviour

- Gases which do not follow the ideal gas equation (*i.e.*, $PV = nRT$) and other gas laws at all temperatures and pressures are called *real gases*.
- Gases show deviation from ideal behaviour at high pressure and low temperature, due to the following :
  - The volume of the gas molecules cannot be neglected in comparison to the volume of the gas.
  - There is considerable force of attraction between the gas molecules and consequently at high pressure and low temperature, molecules are close together.

- By applying pressure and volume correction to the ideal gas equation, van der Waals equation for real gases is obtained,

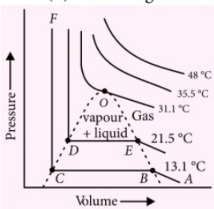
$$\left[P+\frac{n^2a}{V^2}\right][V-nb]=nRT$$

Volume correction = $(V - b)$

Pressure correction = $P+\dfrac{a}{V^2}$

[∵ for 1 mole of gas]

- Unit of a : atm L^2 mol^{-2}
  Unit of b : L mol^{-1}
- **Significance of van der Waals constants :**
  - 'a' is a measure of the magnitude of the attractive forces among the gas molecules.
  - 'b' is a measure of the effective size of the gas molecules, and its value is equal to four times the actual volume of the gas molecules.
  - Higher the value of a, more easily the gas will be liquefied.
- A gas can be liquefied by (i) increasing the pressure and (ii) decreasing the temperature.



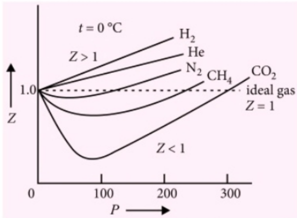
Isotherms for carbon dioxide showing critical region

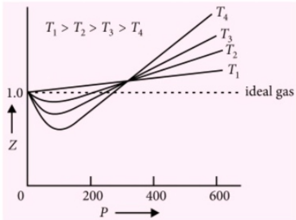
- The extent to which a real gas deviates from ideal behaviour is known as *the compressibility factor,*

$$Z=\frac{PV}{RT} \qquad (\because n=1)$$

Key Points

For ideal gases, $Z = 1$ and for real gases, $Z \neq 1$
When $Z < 1$, it is negative deviation and the gas is more compressible than expected from ideal behaviour.
When $Z > 1$, it is positive deviation and the gas is less compressible than expected.





- The maximum temperature at which a gas can be liquefied by the application of pressure alone is called the *critical temperature,* T_c.
- The minimum pressure required to liquefy the gas at the temperature T_c is called the *critical pressure,* P_c.
- The volume occupied by one mole of the gas at critical temperature, T_c and critical pressure, P_c is called the *critical volume* (V_c) of the gas.

Key Points

- Relationship between velocities :

$$c_{rms}:c_{av}:c_{mp}=\sqrt{3}:\sqrt{8/\pi}:\sqrt{2}$$
$$= 1.224 : 1.128 : 1$$

- Critical temperature, $T_c=\dfrac{8a}{27Rb}$
- Critical pressure, $P_c=\dfrac{a}{27b^2}$
- Critical volume, $V_c = 3b$
- Relationship between critical constants :

$$P_cV_c=\frac{3}{8}RT_c$$

LIQUID STATE

- Liquid state is intermediate between gaseous and solid states. They possess fluidity like gases but incompressibility like solids.

Properties of Liquids

- **Diffusion :** It is the process of intermixing of the molecules of two or more liquids to form a homogeneous mixture or solution.
  Rate of diffusion ∝ Temperature
- **Evaporation :** It is the process of conversion of a liquid into its vapours at room temperature.
  Rate of evaporation ∝ Temperature and surface area
- **Vapour pressure :** It is defined as the pressure exerted by the vapours in equilibrium with the liquid at a given temperature.
  - At any given temperature, the vapour pressure of different liquids is different because their cohesive forces differ.
  - It depends upon the (i) nature of liquid and (ii) temperature of liquid.
  - Vapour pressure of a liquid at two different temperatures is expressed by the Clausius-Clapeyron equation :

$$\log\frac{P_2}{P_1}=\frac{\Delta_{vap.}H}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

- **Surface tension :** It is the force per unit length acting perpendicular to the tangential line drawn on the surface of the liquid.
  - Units of surface tension : dynes cm^{-1}
  - SI unit : N m^{-1}
  - It is denoted by γ.
- **Effect of temperature on surface tension of liquid :**
  - The intermolecular attractive forces (which are responsible for surface tension) are comparatively smaller at higher temperature, hence surface tension decreases with rise in temperature.
- Surface tension of liquid is measured by the drop count method using a stalagmometer.
- Let γ_1 and d_1 be the surface tension and density of water and γ_2 and d_2 be surface tension and density of the liquid whose surface tension is to be determined.

$$\frac{\gamma_1}{\gamma_2}=\frac{n_1 d_2}{n_2 d_1}$$

- **Viscosity :** It is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows.
  - Force of friction 'f' between two cylindrical layers each having area 'A' cm^2 separated by a distance 'x' cm and having a velocity difference 'v' cm/sec is given by

$$f\propto A\frac{v}{x};\quad f=\eta A\frac{v}{x}$$

(η = viscosity coefficient)

- Viscosity is generally determined by Ostwald's method using viscometer.

$$\frac{\eta}{\eta_w}=\frac{d\times t}{d_w\times t_w}$$

where η_w and η = coefficient of viscosity of water and liquid respectively, d = density of liquid d_w = density of water; t = time of flow of liquid; t_w = time of flow of water.

- **Effect of temperature on viscosity of liquid :** In general, the viscosity decreases with increase in temperature because at high temperature, molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.
  - The variation of viscosity (η) with temperature can be expressed by the following relationship : $\eta = Ae^{-E_a/RT}$
    where A and E_a are constants. E_a is called *activation energy* and A is called *pre-exponential factor*.

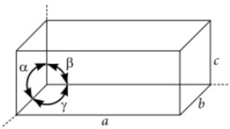
SOLID STATE

- Solids have high density and low compressibility as compared to gas as well as liquid phase.

Solid state

- Crystalline solids (sharp melting point) → High degree of internal order which extends throughout the crystal **Long range order** (*e.g.* NaCl)
- Amorphous solids (do not have sharp melting point) → Do not have long range order but have **short range order.** (*e.g.* Rubber, silica, etc.)

- **Crystal :** Solid figure which has a definite geometrical shape with flat faces and sharp edges.
- **Classification of crystals based on bond types :**
  - **Molecular crystals (van der Waals crystals):** Composed of aggregates of discrete molecules held together by van der Waals forces.
  - **Ionic crystals :** Involves electrostatic forces.
  - **Covalent crystals :** Forces of chemical nature extend in 3-dimension.
  - **Metallic crystals :** Electrons are loosely held.
- **Types of symmetry in crystals :**
  (i) Centre of symmetry, (ii) Plane of symmetry
  (iii) Axis of symmetry, (iv) Elements of symmetry
- **Space lattice :** 3D-translational repetition of the centres of gravity of the unit of pattern in the crystal by means of points (lattice points).
- **Unit cell :** Cuboid obtained by connecting the lattice point such that each parallelopiped contains a complete unit of pattern of the crystal.



A unit cell

It is the smallest structure of which the crystalline solid (or crystal) is built by its repetition in the 3-dimension.

- The crystal lattices of the substances may be categorised into seven types. These are called *Bravais lattices*. These unit cells are characterised by following parameters :
  - Relative length of the edges along the three axes (a, b, c).
  - The three angles between the edges (α, β, γ).

Crystal system	Relative axial length	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, CsCl, CaF_2, CaO
Tetra-gonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	K_2PtCl_6, $PbWO_4$, NH_4Br
Ortho-rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	K_2SO_4, KNO_3, $BaSO_4$, $CaCO_3$ (aragonite)
Rhombo-hedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$CaCO_3$ (calcite), $NaNO_3$
Hexa-gonal	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	AgI, SiC, HgS
Mono-clinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	$CaSO_4 \cdot 2H_2O$, $KClO_3$, $K_4[Fe(CN)_6]$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$

Three Types of Cubic Crystals

- **Simple cubic unit cell :** Points only at the corners
- **Body-centred cubic unit cell :** Points at the centre of the cube and at the corners
- **Face-centred cubic unit cell :** Points at the centre of each of the six faces of the cube apart from the points at the corners.
- For simple cubic, number of atoms in a unit cell = 1
  For *bcc*, number of atoms in a unit cell = 2
  For *fcc*, number of atoms in a unit cell = 4

Coordination Number

- It is the number of nearest neighbours or spheres in contact with the sphere under consideration.
- Coordination number of a crystal depends upon its structure.
  - Simple cubic structure has CN = 6
  - Face centred cubic structure (*fcc*) has CN = 12
  - Body centred cubic structure (*bcc*) has CN = 8

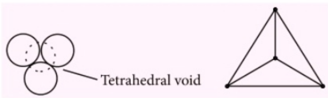
Close packing in crystals

- **In 2-Dimension :**

Arrange-ment type	Name	% efficiency	Coordination number
AAAA........	Square close packing	52.4%	4
ABAB..........	Hexagonal close packing	60.4%	6

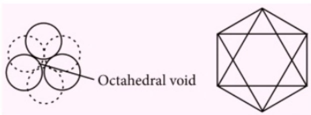
- **In 3-Dimension :**
  - **Square close packing :** *AAA* .... type called simple cubic packing.
  - **In the case of hexagonal packing** alternate voids are filled and in the second layer there are two types of voids :

Tetrahedral voids are holes or interstices surrounded by four spheres present at the corners of a tetrahedron.



CN of tetrahedral void is 4.

Octahedral voids are holes surrounded by six spheres located on a regular octahedron.



CN of octahedral void is 6.

- If there are N spheres, then
  Number of tetrahedral voids = $2N$
  Number of octahedral voids = N

Size of voids : Cubic void > Octahedral void > Tetrahedral void

Arrangement in III layer	Name	Efficiency
ABAB....	Hexagonal close packing (*hcp*)	74%
ABCABC......	Cubic close packing (*ccp*) or face-centred cubic arrangement (*fcc*)	74%

- **Limiting radius ratio :** It is the ratio of the radii of positive and negative ions in a crystal.

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}} = \frac{r_+}{r_-}$$

- **Limiting radius ratio, coordination number and geometry**

r_+/r_-	C.N.	Geometry
< 0.155	2	linear
0.155 - 0.225	3	plane triangular
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.000	8	cubic (body centred)

- For a tetrahedral void, $r = 0.225\ R$
  For an octahedral void, $r = 0.414\ R$
  where r is the radius of the void and R is the radius of the sphere in close packing.

- Density of the crystal $(\rho) = \dfrac{Z \times M}{a^3 \times N_0}$
  where,
  Z = number of atoms per unit cell (for element)
  = number of formula units per unit cell (for ionic compounds)
  M = atomic weight of elements/ formula weight of ionic compounds
  a = edge length

Packing in Solids

- *Packing fraction* (density of packing) = v/V
  where v = volume of the spherical atom $= \frac{4}{3}\pi r^3$
  V = volume of the cube $= a^3$

  For simple cubic, $r = \dfrac{a}{2}$;

  Packing fraction $= \dfrac{\pi}{6} = 0.52$

  For *bcc*, $r = \dfrac{\sqrt{3}a}{4}$;

  Packing fraction $= \dfrac{\sqrt{3}\pi}{8} = 0.68$

  For *fcc*, $r = \dfrac{a}{2\sqrt{2}}$;

  Packing fraction $= \dfrac{\sqrt{2}\pi}{6} = 0.74$

- For simple cubic, $d = a$;
  For *bcc*, $d = \dfrac{\sqrt{3}a}{2}$; For *fcc*, $d = \dfrac{a}{\sqrt{2}}$
  where d is the distance of nearest neighbours and a is the edge length of cubic unit cell.

- **Bragg's equation :** $n\lambda = 2d\sin\theta$
  where d is the distance between atomic layers in a crystal, λ is the wavelength of the incident X-ray beam, n is an integer, θ is the angle of incidence.

Imperfections in Solids

- Any deviation from the perfect atomic arrangement in a crystal is called *imperfection* or *defect*.

Point Defects

- They are the deviations which exist from the regular (or periodic) arrangements around an atom or a group of atoms in a crystalline substance.
- **Types of point defects :**
  - Stoichiometric defects
  - Non - stoichiometric defects
  - Impurity defects

Stoichiometric Defects

- The compounds in which the number of cations and anions are exactly in the same ratio as represented by their chemical formula are called *stoichiometric compounds.*
- The defects that do not disturb the ratio of cations and anions are called *stoichiometric defects.*
- **These are of two types :**
  - **Schottky defect :** If in an ionic crystal of the type A^+B^-, equal number of cations and anions are missing from their lattice.
    - As the number of ions decreases as a result of this defect, density of the solid decreases.
  - **Frenkel defect :** If an ion is missing from its correct lattice sites (causing a vacancy or a hole) and occupies an interstitial site, electrical neutrality as well as stoichiometry of the compounds are maintained.
    - As no ions are missing from the crystal lattice as a whole, therefore density of the solid remains the same.

Non - Stoichiometric Defects

- If as a result of imperfection, the ratio of number of cations to anions becomes different from that indicated by the ideal chemical formula, the defects are called *non-stoichiometric defects.*
  - These defects arise either due to excess of metal atoms or non-metal atoms or presence of impurities/foreign particles.
  - **Metal excess defects due to anion vacancies :** A compound may have excess metal ion if a negative ion is absent from its lattice site leaving a hole which is occupied by electron to maintain neutrality.
    - The holes that are occupied by electrons are called **'F' centres** (or **colour centres**) and are responsible for the colour of the compound and many interesting properties.
  - **Metal excess defects due to interstitial cations :** Metal excess may also be caused by an extra cation (positive ion) present in an interstitial site. Electrical neutrality is maintained by presence of an electron in another interstitial site. This defect is similar to Frenkel defect and is found in crystals having *Frenkel defects.*
  - **Metal deficiency due to cation vacancies :** The non-stoichiometric compounds may have metal deficiency due to the absence of a metal from its lattice site. The charge is balanced by an adjacent ion having higher positive charge. This type of defect are generally shown by compounds of *transition elements.*
  - **Point defects due to the presence of foreign atoms :** These defects arise when foreign atoms are present at the lattice site (in place of host atoms) or at the vacant interstitial sites. In the former case, substitutional solid solutions are obtained. The formation of former depends upon the electronic structure of the impurity while that of latter on the size of the impurity.

Electrical and Magnetic Properties

- **Electrical properties :** Solids may be classified into three categories depending upon their values of electrical conductivity.
  - **Conductors :** Electrical conductivity, 10^4 to 10^7 ohm^{-1} m^{-1}
  - **Insulators :** Electrical conductivity, 10^{-20} to 10^{-10} ohm^{-1} m^{-1}

- **Semiconductors :** Electrical conductivity, 10^{-6} to 10^4 ohm^{-1} m^{-1}
  - ***n*-type semiconductors :** Group 14 elements doped with group 15 elements, free electrons increase conductivity.
  - ***p*-type semiconductors :** Group 14 elements doped with group 13 elements, holes increase conductivity.

- **Magnetic properties :** Solid substances are classified into following categories depending upon their behaviour towards magnetic field.
  - **Diamagnetic substances :** Substances which are weakly repelled by external magnetic field. *e.g.* N_2, NaCl, Zn, TiO_2, etc.
  - **Paramagnetic substances :** Substances which are weakly attracted by external magnetic field. *e.g.* O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}, etc.
  - **Ferromagnetic substances :** Substances which show permanent magnetism even in the absence of external magnetic field. *e.g.* Ni, Fe, Co, etc.
  - **Antiferromagnetic substances :** Substances which have zero net dipole moment even though they are having large number of unpaired electrons. *e.g.* MnO.
  - **Ferrimagnetic substances :** These are the substances which possess very small net magnetic moment even though they are having a large number of unpaired electrons. *e.g.* Fe_3O_4.

ATOMIC STRUCTURE

- Introduction
- Atomic Spectra
- Bohr's Atomic Model
- Schrodinger Wave Equation and Concept of Atomic Orbital
- Quantum Numbers

TIPS TO REMEMBER

- Dalton's atomic theory proposed that matter is composed of small, indivisible particles called *atoms*.
- However, atoms are further composed of fundamental particles *i.e.*, *electrons*, *protons* and *neutrons*.
- Electron and proton were discovered by passing electric discharge through discharge tube under high pressure and low temperature.
  - Invisible rays travelling from cathode to anode producing fluorescence indicated the presence of electrons in atoms.
  - Anode rays moving from anode to cathode suggested the presence of positively charged protons.
- Neutrons were discovered by bombarding a thin sheet of beryllium element with α-particles.

Properties of electron, proton and neutron

Properties	Electron, *e*	Proton, *p*	Neutron, *n*
Mass	9.101×10^{-31} kg	1.67262×10^{-27} kg	1.67495×10^{-27} kg
Charge	-1.6022×10^{-19} C	$+1.6022 \times 10^{-19}$ C	0
Mass relative to the electron	1	1836	1839
Spin	1/2	1/2	1/2
Charge relative to the proton	−1	+1	0
Discovery	Thomson	Goldstein	Chadwick

- According to Thomson's atomic model, an atom consists of a uniform sphere in which positive charge is uniformly distributed. The electrons are embedded into it in such a way so as to give the most stable electrostatic arrangement.
- Rutherford discovered the nucleus by bombarding a thin gold foil by fast moving α-particles.
- **Atomic number :** It is the number of protons present in the nucleus of an atom.

- **Mass number :** It is the total number of protons and neutrons (called *nucleons*) in an atom.
- **Isotopes :** These are different atoms of the same element having same atomic number but different number of neutrons. *e.g.*, ^1_1H; ^2_1D; ^3_1T and $^{35}_{17}Cl$; $^{37}_{17}Cl$
- **Isobars :** These are atoms of different elements having same mass number but different number of protons. *e.g.* $^{18}_{40}Ar$, $^{19}_{40}K$, $^{20}_{40}Ca$.
- **Isotones :** These are atoms of different elements having same number of neutrons. *e.g.*, $^{14}_6C$; $^{15}_7N$' $^{16}_8O$.
- **Isodiapheres :** These are atoms having same difference in number of neutrons and protons. *e.g.*, $^{235}_{92}U$ and $^{231}_{90}Th$; $^{39}_{19}K$ and $^{19}_9F$.
- Waves having both electric and magnetic fields associated with them are referred to as *electromagnetic radiations*, and the arrangement of different types of electromagnetic radiations in the order of increasing wavelengths or decreasing frequencies is known as *electromagnetic spectrum.*
- **Electromagnetic spectrum :**

  cosmic rays, γ-rays, X-rays, UV, visible, IR, microwaves, radiowaves

  (increasing wavelength or decreasing frequency)
- Electromagnetic waves are considered to have *dual nature i.e.*, particle nature and wave nature.
- Wave nature of matter can be characterised by the following parameters :

  (i) Wavelength (λ), (ii) Frequency (υ),

  (iii) Velocity (c), (iv) Amplitude (a)

  (v) Wave number ($\bar{\upsilon}$)

  $$\upsilon = \frac{c}{\lambda} = c\bar{\upsilon} \text{ as } \frac{1}{\lambda} = \bar{\upsilon}$$
- Moseley's equation gave a relationship between frequency and atomic number :

  $$\sqrt{\upsilon} = a(Z - b)$$

  where υ = frequency, Z = nuclear charge and a and b are constants.
- Particle nature of electromagnetic radiation could be explained in terms of black body radiation and Planck's quantum theory.
- An object which perfectly absorbs and emits radiations is known as *black body* and the radiation emitted is called *black body radiation.*
- When light of a suitable frequency strikes on a metal surface, electrons are emitted from it. This phenomenon is known as *photoelectric effect* and the emitted electrons are known as *photoelectrons.*

  Metals having low ionisation energies like Cs, Rb, ..., etc. exhibit photoelectric effect.
- A few observations regarding the photoelectric effect are :
  - A minimum frequency of light, known as the *threshold frequency* (υ_0) is needed to eject the electrons.
  - Kinetic energy of the ejected electron is directly proportional to the frequency of the incident light and independent of the intensity.
  - Number of electrons ejected depends upon the intensity of incident light but not on its frequency.
- These observations were explained on the basis of Planck's quantum theory according to which radiant energy emitted or absorbed is always quantised and in case of light, each quantum of energy is known as *photon.*

  $$E \propto \upsilon \quad \text{or} \quad E = h\upsilon \quad \text{or} \quad E = nh\upsilon$$

  where h = Planck's constant = 6.63×10^{-34} J s and n = 1, 2, 3, ...

  Also $E = \dfrac{hc}{\lambda}$ $\quad [\because \upsilon = \dfrac{c}{\lambda}]$
- Photoelectric effect can be mathematically expressed on the basis of quantum theory as :

  $$\frac{1}{2}mv^2 = h(\upsilon - \upsilon_0)$$

  where $\frac{1}{2}mv^2$ = kinetic energy of ejected electrons

  υ = frequency of incident light

  υ_0 = threshold frequency

Atomic Spectra

- Splitting of light into a series of coloured bands is known as *dispersion* and the series of coloured bands is known as *spectrum*. Spectrum could be continuous *i.e.* the different colours merge with one another or discontinuous *i.e.* having discrete lines.

- Atomic spectra is of two types :
  (i) Emission spectra (ii) Absorption spectra
- The hydrogen atom spectrum is an emission spectrum consisting of well defined lines and hence is also referred to as *line spectra*.
- A general expression for the spectrum is :

$$\frac{1}{\lambda} = \bar{\upsilon} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad (n_2 > n_1)$$

  R = Rydberg constant = 109677 cm^{-1}
  Z = atomic number
- Different spectral lines in the spectrum of hydrogen atom :

Series	Region	n_1	n_2
Lyman	Ultraviolet	1	2, 3, 4, 5 ...
Balmer	Visible	2	3, 4, 5, 6 ...
Paschen	Infra-red	3	4, 5, 6, 7 ...
Brackett	Infra-red	4	5, 6, 7, 8 ...
Pfund	Infra-red	5	6, 7, 8, 9 ...

Bohr's Atomic Model

- The main postulates are
  (i) Atom consists of a small, heavy and positively charged nucleus in centre, and electrons revolve around the nucleus in fixed paths called *orbits*.
  (ii) Energy of an electron in the orbit does not change with time.
  (iii) The electron can revolve only in those orbits whose angular momentum is an integral multiple of $h/2\pi$ *i.e.*,

$$mvr = \frac{nh}{2\pi}, \quad n = 1, 2, 3, \ldots.$$

  (iv) When electron jumps from one level to another, energy is either emitted or absorbed.
  The energy difference between two states is given by

$$\Delta E = E_2 - E_1$$

  As the distance of the orbits increases from the nucleus, the energy gap goes on decreasing, *i.e.*,

$$E_2 - E_1 > E_2 - E_3 > E_3 - E_4 > \ldots\ldots$$

- Energy of n^{th} orbit,

$$E_n = -R_H\left(\frac{Z^2}{n^2}\right), \quad n = 1, 2, 3, \ldots.$$

$$E_n = \frac{-2\pi^2 me^4 Z^2}{n^2h^2} = \frac{-2.18\times10^{-18}\times Z^2}{n^2}\ \text{J/atom}$$

$$= \frac{-1312Z^2}{n^2}\ \text{kJ mol}^{-1}$$

  Here Z = nuclear charge for H-atom and single electron species like He^+, Li^{2+}, Be^{3+}, ..., etc.
- Bohr's radius

$$r = \frac{n^2h^2}{4\pi^2 mkZe^2}$$

  [k is a constant which is equal to $\frac{1}{4\pi\varepsilon_0}$]
  For H-atom, n = 1, Z = 1. $\therefore$ r = 0.529 Å
  In general, $r_n = \frac{0.529n^2}{Z}$ Å
- Number of waves in n^{th} orbit = $\frac{2\pi r}{\lambda}$
- According to de-Broglie, all moving particles possess wave nature.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \qquad (p = mv)$$

- According to Heisenberg's uncertainty principle,

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

- **Limitations of Bohr's Model**
  - Bohr's model could explain the line spectra of H-atom and hydrogen like species but failed to explain the spectra of multi-electron atoms.
  - It could not explain the splitting of spectral lines into finer lines under the influence of magnetic effect (Zeeman effect) and electric effect (Stark effect).
  - This is not in accordance with de Broglie concept of dual nature of matter and Heisenberg's uncertainty principle.

Key Point

- Velocity of an electron in the nth orbit :

$$v_n = k\frac{2\pi Ze^2}{nh} = 2.18\times10^6\,\frac{Z}{n}\ \text{m s}^{-1}$$

Key Points

- Energy of an electron for H-like atom :

$$= -13.6 \times \frac{Z^2}{n^2} \text{ eV per atom}$$

$$= -1312 \times \frac{Z^2}{n^2} \text{ kJ mol}^{-1}$$

- Number of spectral lines : $= \frac{n(n-1)}{2}$

Schrodinger Wave Equation and Concept of Atomic Orbitals

- Behaviour of electrons around the nucleus was explained by Schrodinger, in the form of Schrodinger's wave equation :

$$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

- ψ is the wave function and gives the amplitude of the electron wave.
- ψ^2 is the probability density or probability amplitude and gives the probability of finding the electron at a point in the atom.
- An *orbital* is a region around the nucleus where the probability of finding electron is maximum.

Quantum Numbers

- Each electron in an atom can be identified by a set of four quantum numbers.
  - **Principal quantum number, n :** It corresponds to the main energy level or shell in which the electron is present.

The value of n :	1	2	3	4
Corresponding shell :	K	L	M	N

  - **Azimuthal quantum number, l :** It gives the orbital angular momentum and corresponds to the subshell in a given principal energy shell.

    $l = 0, 1, 2, 3, ..., (n - 1)$

    The various subshells are designated by the letters s, p, d, f.

The value of l :	0	1	2	3
Designation :	s	p	d	f

  - **Magnetic quantum number, m_l :** It describes the behaviour of an electron in magnetic field and it corresponds to the number of orbitals in a subshell.

    $m_l = -l$ to 0 to $+l = (2l + 1)$ values.

Subshell :	s	p	d	f
No. of orbitals :	1	3	5	7

  - **Spin quantum number, m_s :** It corresponds to the direction of electron spin in each orbital.

    m_s can have only two values, *i.e.*, $\pm 1/2$, represented as $\uparrow$ and $\downarrow$.

Key Points

- The point where there is zero probability of finding an electron is called *nodal point* or *node*.
- For an atom of principal quantum number, n, there are
  - $(n - l - 1)$ radial nodes
  - l angular nodes
  - total $(n - 1)$ nodes.

- Electrons are distributed in different orbitals in an atom and this arrangement is referred to as *electronic configuration*.
- The filling up of electrons in different orbitals is based on the following rules :
  - **Aufbau's principle :** Electrons are progressively added to the different orbitals in their increasing order of energy.

    $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < ....$
  - **Pauli's exclusion principle :** No two electrons in an atom can have the same set of all the four quantum numbers.
  - **Hund's rule of maximum multiplicity :** Electron pairing in an orbital of same energy takes place only when each orbital is singly filled.

CHEMICAL BONDING AND MOLECULAR STRUCTURE

- Ionic, Covalent and Coordinate Bond
- Bond Parameters
- Resonance
- VSEPR Theory
- VBT
- Hybridisation
- MOT

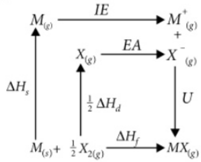
TIPS TO REMEMBER

- The process of combination of atoms, called *chemical bonding* involves the union of two or more atoms through redistribution of electrons to acquire minimum energy.

- Kossel and Lewis proposed the electronic theory of chemical bonding according to which atoms achieve stable octet when they are linked by chemical bonds.
- Atoms combine together either by transferring valence electrons or by sharing of valence electrons.
- The attainment of noble gas configuration, $ns^2\ np^6$, in the valence shell is the driving force behind the formation of chemical bonds.
- There are mainly three types of bonds :
  (i) Ionic bond, (ii) Covalent bond,
  (iii) Coordinate bond

Ionic Bond

- The bonds formed between atoms by transferring of valence electrons from one atom to another is said to be *electrostatic* or *ionic bond*, and the compound so formed is an *ionic compound.*
- **Conditions for formation of electrovalent bond**
  - **Number of valence electrons :** The atom which changes to a cation must contain 1, 2 or 3 electrons and the one changing to anion must contain 5, 6 or 7 valence electrons.
  - **Electronegativity difference :** Higher the electronegativity difference between the atoms, more ionic will be the bond.
  - **Low ionisation energy :** Ionisation energy of the element forming the cation, *i.e.*, metal, should be low.
  - **High electron affinity :** Electron affinity of the element forming anion, *i.e.*, non-metal, should be high.
  - **High lattice energy :** Higher the lattice energy, greater is the ease of formation of ionic compound.
- **Characteristics of ionic compounds**
  - They are usually crystalline solids.
  - Have high melting and boiling points by virtue of strong electrostatic forces of attraction between the ions.
  - They are usually soluble in polar solvents having high dielectric constant like water.
  - They are usually good conductors of electricity in solution or molten state. However, they do not conduct in the solid state because of strong forces between the ions.
- **Born-Haber cycle**
  The Born-Haber cycle involves the formation of an ionic compound from the reaction of a metal (often a group I or group II element) with a non-metal. Born-Haber cycles are used primarily as means of calculating lattice energies, which cannot be measured directly.
  This cycle is based on Hess's law, *i.e.* the formation of an ionic crystal may occur either by direct combination of the elements or by an alternate process in which various steps are involved.



$$\Delta H_f = +\ \Delta H_s + IE + \frac{1}{2}\Delta H_d - EA - U$$

where ΔH_f = Enthalpy of formation,
ΔH_s = Enthalpy of sublimation,
IE = Ionisation energy,
ΔH_d = Enthalpy of dissociation,
EA = Electron affinity and U = Lattice energy.
The enthalpies of sublimation and dissociation and the ionization energy are positive since energy is supplied to the system. The electron affinity and lattice energy are negative since energy is evolved in these processes.

Covalent Bond

- Bond formed by mutual sharing of electrons between the combining atoms is called *covalent bond.*
- In molecules having multiple covalent bonds, if atoms share
  - one electron pair; single covalent bond is formed.
  - two electron pairs; double covalent bond is formed.
  - three electron pairs; triple covalent bond is formed.

- **Characteristics of covalent compounds**
  - They usually exist as gases or liquids due to presence of weak van der Waals forces between the atoms.
  - Except SiC, SiO_2 and diamond, almost all the covalent compounds have lower melting and boiling points.
  - They are poor conductors of electricity. However, covalent compounds like HCl possessing polar nature can conduct electricity.
- Formal charge $= V - L + \frac{1}{2}S$

  where V = total number of valence electrons in the free atom, L = total number of lone pairs, S = total number of bond pairs.

Coordinate Bond

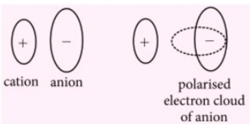
- A covalent bond in which both electrons of the shared pair are contributed by one of the atoms, is called a *coordinate bond* or *dative bond*.
- Atom contributing the electron pair is called the *donor atom* and the one accepting the electron pair is called the *acceptor atom*.
- A covalent bond in which the bond pair is unequally shared such that the atoms acquire a partial positive and negative charge is called a *polar covalent bond*.
- Percentage of ionic character

  $= [16(X_A - X_B) + 3.5(X_A - X_B)^2]$
- Dipole moment, $\mu = q \times d$.

  Unit of μ is Debye (D),

  1 D $= 10^{-18}$ esu cm $= 3.33 \times 10^{-30}$ C m

  $$\% \text{ Ionic character} = \frac{\mu_{obs.}}{\mu_{ionic}} \times 100$$
- **Fajan's rule :** In ionic bond, some covalent character is introduced because of the tendency of the cation to polarise the anion. In fact cation attracts the electron cloud of the anion and pulls electron density between two nuclei.



According to Fajan's rule, the magnitude of covalent character in the ionic bond depends upon the extent of polarisation caused by cation. In general,

- Smaller the size of cation, larger is its polarising power.
- Larger the anion, more will be its polarisability.
- More charge on cation and anion, more is the covalent character.
- Cations having 18 electrons in outermost shell bring greater polarisation.

Bond Parameters

- **Bond length :** It is the equilibrium distance between the nuclei of two bonded atoms in a molecule.
  - **Covalent radius :** It is the radius of the core of an atom in contact with the core of an adjacent atom in a bonded situation.
  - **van der Waals radius :** It is half the distance between two similar adjacent atoms belonging to two nearest neighbouring molecules of the same substance in solid state.
- **Bond angle :** It is the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.
- **Bond enthalpy :** It is the amount of energy required to break one mole of bonds of a particular type between the atoms in the gaseous state.
- **Bond order :** It is given as the number of bonds between the atoms in a molecule.

Resonance

- Whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately, and the structure is called *resonance hybrid*.

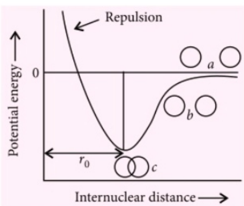
Valence Shell Electron Pair Repulsion (VSEPR) Theory

- According to this theory, bonded atoms in a molecule adopt that arrangement around the central atom which keeps them as far apart as possible.
- **Postulates**
  - Shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.
  - Electron pairs in the valence shell repel one another and the order of repulsion is :

    $$lp - lp > lp - bp > bp - bp$$
  - Electron pairs tend to occupy such positions in space that minimise repulsion and maximise distance between them.
  - Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

Valence Bond Theory (VBT)

- This theory was developed by Heitler and London and latter developed by Pauling. Its main postulates are :
  - Bond is formed due to interaction of valence electrons. The core electrons do not participate in bond formation.
  - During bond formation, only valence electrons lose their identity.
  - Bond formation is accompanied by release of energy, and this accounts for the stability of the bond.
  - The molecule has minimum energy at the equilibrium distance known as the *intermolecular distance*. Larger the decrease in energy, stronger will be the bond formed.



- When two atoms approach each other, overlapping of atomic orbitals takes place to give molecular orbitals.
- Sigma (σ) bond is formed by the head on overlap of the atomic orbitals along the internuclear axis. This type of combination is shown by *s-s*, *s-p* and *p-p* overlapping.
- Pi (π) bond is formed by lateral overlap of half-filled atomic orbitals perpendicular to the internuclear axis. Such an overlapping is exhibited only by *p*-orbitals.

Hybridisation

- The process of mixing of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy is known as *hybridisation*.
- The features of hybridisation are as follows :
  - Number of hybrid orbitals = Number of orbitals undergoing hybridisation
  - Hybrid orbitals are always equivalent in energy and shape.
  - Hybrid orbitals are more effective in forming stable bonds.
  - Hybrid orbitals are directed in space in preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Thus, the type of hybridisation indicates the geometry of the molecules.
- The important conditions for hybridisation are :
  - Only those orbitals which are present in the valence shell of the atom are hybridised.
  - Orbitals undergoing hybridisation should have nearly same energies.
  - Promotion of electron is not essential before hybridisation occurs.

SHAPES OF SOME SIMPLE MOLECULES

Type of molecule	No. of electron pairs	No. of bond pairs	No. of lone pairs	Type of hybridisation involved	Geometry of molecule	Examples
AB_2	2	2	0	sp	Linear	BeF_2, $[Ag(NH_3)_2]^+$
AB_3	3	3	0	sp^2	Trigonal planar	BF_3, $AlCl_3$
AB_2L	3	2	1	sp^2	V-shaped	$SnCl_2$, $PbCl_2$
AB_4	4	4	0	sp^3	Tetrahedral	CH_4, SiF_4, CCl_4
AB_3L	4	3	1	sp^3	Trigonal pyramidal	NH_3, PX_3 (X = F, Cl, Br, I)
AB_2L_2	4	2	2	sp^3	V-shaped	H_2O, OF_2, SCl_2
AB_5	5	5	0	sp^3d	Trigonal bipyramidal	PF_5, PCl_5, $SbCl_5$
AB_4L	5	4	1	sp^3d	See saw	SF_4, $TeBr_4$
AB_3L_2	5	3	2	sp^3d	T-shaped	ClF_3, $XeOF_2$
AB_2L_3	5	2	3	sp^3d	Linear	XeF_2, ICl_2^-, I_3^-
AB_6	6	6	0	sp^3d^2	Octahedral	SF_6
AB_5L	6	5	1	sp^3d^2	Square pyramidal	IF_5, ClF_5, BrF_5
AB_4L_2	6	4	2	sp^3d^2	Square planar	XeF_4, ICl_4^-
AB_7	7	7	0	sp^3d^3	Pentagonal bipyramidal	IF_7, XeF_6

Molecular Orbital Theory (MOT)

- Electrons in a molecule are present in molecular orbitals just as the electrons of atoms are present in atomic orbitals.
- Atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital, it is influenced by two or more nuclei depending upon the number of atoms in the molecule.
- Number of molecular orbitals formed is equal to the number of combining atomic orbitals.
  - The molecular orbital having energy lower than the parent atomic orbital is known as *bonding molecular orbital.*
  - Molecular orbital having energy greater than the parent atomic orbital is known as *antibonding molecular orbital.*
- Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.
- The molecular orbitals are filled in accordance with the Aufbau's principle, Pauli's exclusion principle and Hund's rule.
- Order of energy of molecular orbitals for elements with $Z \leq 7$

  $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x \approx \pi 2p_y < \sigma 2p_z < \pi^* 2p_x \approx \pi^* 2p_y < \sigma^* 2p_z$

  Order of energy of molecular orbitals for elements with $Z \geq 8$

  $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x \approx \pi 2p_y < \pi^* 2p_x \approx \pi^* 2p_y < \sigma^* 2p_z$

CONCEPT MAP

s-BLOCK ELEMENTS [Last e^- enters into ns orbit]

Group 1 or IA : Alkali Metals

(Li, Na, K, Rb, Cs, Fr)
[Fr-Radioactive]

Electronic configuration

[Noble gas]ns^1

Li shows anomalous behaviour and has diagonal relationship with Mg (group 2).

Biological importance

- Na^+ in blood plasma and other interstitial fluids.
- K^+ inside the cells, important for Na^+ - K^+ pump.

Physical properties

- All elements are metals, excellent conductors of electricity, soft and highly reactive.
- Hydration enthalpy: Li^+ has maximum degree of hydration.
- Strongly electropositive
- Exhibit +1 oxidation state
- Monovalent
- $(IE)_1$ is lowest.
- $(IE)_2$ is very high.
- Weak metallic bonds
- Low melting and boiling points
- Paramagnetic
- Form ionic compounds
- Li, Na, K - lighter than water
- Flame colouration: Li-crimson, Na-yellow, K-pale violet, Rb-red violet, Cs -blue
- Exhibit photoelectric effect (except Li)

Chemical properties

- Strong reducing agents
  In gaseous state: Li < Na < K < Rb < Cs
  In aqueous solution: Na < K < Rb < Cs < Li
- Vigorous reaction with water (except Li).
- All tarnish in air, form oxides or hydroxides on the surface. With excess of air, Li forms monoxide (Li_2O); Na forms peroxide (Na_2O_2); K, Rb and Cs form superoxide. (MO_2)
- Oxides and hydroxides are highly basic.
- Form crystalline ionic hydrides (M^+H^-).
- Form alloys but weak tendency to form complexes (except Li).
- Only Li forms nitride, Li_3N.
- Soluble in liquid NH_3
  $M + (x+y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$
- All react directly with halogens to form ionic halides (except Li).

Important compounds

$Na_2CO_3 \cdot 10H_2O$
Sodium carbonate (washing soda)
- Manufactured by Solvay process
- Used in softening hard water, cleaning, paints, soap, glass, petroleum and metal refining, paper and textile industry
- Fusion mixture : $Na_2CO_3 + K_2CO_3$

$NaHCO_3$
Sodium hydrogencarbonate (baking soda)
- Prepared by Solvay process
- Used in fire extinguishers, used as antiseptic, antacid, in preparation of baking powder.

NaCl
Sodium chloride (common salt)
- Obtained by evaporation of sea water
- Used in preparation of Na_2CO_3, NaOH, Na_2O_2

NaOH
Sodium hydroxide (caustic soda)
- Manufactured by Castner and Kellner's cell or mercury cathode cell.
- Used in preparation of soap, paper, rayon, pure fats, oils, dyes, mercerising cotton fabrics, petroleum refining.

Group 2 or IIA: Alkaline Earth Metals

(Be, Mg, Ca, Sr, Ba, Ra)
[Ra-Radioactive]

Electronic configuration

[Noble gas] ns^2

Be shows anomalous behaviour and has diagonal relationship with Al (group 13).

Biological importance

- Mg^{2+} as catalyst in enzymatic reactions, present in chlorophyll-*a*
- Ca^{2+} present in bones and teeth enamel, important for blood clotting.

Chemical properties

- Be $\rightarrow$ least reactive,
  Ba and Ra $\rightarrow$ most reactive.
  Ca, Ba, Sr $\rightarrow$ stored in paraffin
- Weaker reducing agents than group 1.
- Be and Mg $\rightarrow$ kinetically inert to O_2 because of formation of an oxide film on their surface.
- Form crystalline ionic solid nitrides (M_3N_2) except Be_3N_2 which is covalent and volatile.
- Hydrides $\rightarrow$ ionic except BeH_2 and MgH_2 (form four 3*c*-2*e* bonds or banana bonds).
- Carbides (MC_2) with C except Be which forms Be_2C (ionic).
- Dissolve in NH_3 $\rightarrow$ dilute solutions bright blue colour, but concentrated solutions, bronze coloured (due to metal clusters).
- Form amalgams and Be, Mg have maximum tendency to form complexes.

Important compounds

$Ca(OH)_2$
Calcium hydroxide (slaked lime)
- Used as building material as mortar (slaked lime + sand + H_2O)
- White washing
- In preparation of NH_3, bleaching powder, glass, tanning industry, purification of sugar.

Physical properties

- They are all silvery white metals, malleable and ductile.
- Ionisation enthalpy
  $\Delta_i H_1$ (group 2) > $\Delta_i H_1$ (group 1)
  $\Delta_i H_2$ (group 1) > $\Delta_i H_2$ (group 2)
- Less electropositive than group 1
- Exhibit +2 oxidation state
- Bivalent
- Less metallic than group 1
- Higher melting and boiling points than group 1
- Diamagnetic
- All (except Be) form ionic compounds
- Density decreases from Be to Ca, increases from Ca to Ba
- Flame colouration : Ca-brick red, Sr-crimson, Ba-apple green, Ra-crimson (Be and Mg do not show flame test)

Portland cement
- Mixture of Ca–silicates and Ca– aluminates with small amount of gypsum.
- CaO = 50-60%, SiO_2 = 20-25%, Al_2O_3 = 5-10%, MgO = 2-3%, Fe_2O_3 = 1-2%, SO_3 = 1-2%
- If lime in excess $\rightarrow$ Cement cracks during settings.
- If lime is less $\rightarrow$ Cement with weak strength.

$CaCO_3$
Calcium carbonate (limestone)
- Used in manufacturing cement [lime stone ($CaCO_3$) + clay (silica and alumina) + gypsum ($CaSO_4 \cdot 2H_2O$)].

$CaSO_4 \cdot 2H_2O$
Calcium sulphate (Gypsum or alabaster or selenite)
- It is shiny like marble and is used to make ornaments.

$Mg(OH)_2$
Magnesium hydroxide (Milk of magnesia)
- Used as an antacid.

$MgCl_2 \cdot 5MgO \cdot xH_2O$
Magnesia cement or Sorel cement
- When a saturated solution of $MgCl_2$ is mixed with MgO, then the paste obtained sets to a hard marble.
- It is used as
  - dental filling.
  - a finish for plaster due to its high polish.
  - for cementing glass and porcelain.
  - for making artificial stones.

$CaSO_4 \cdot 1/2H_2O$
Calcium sulphate hemihydrate (plaster of Paris)
- Used in surgical bandages for fractured bones of the body.
- For producing moulds for pottery and ceramics.

Hydrogen Bonding

- The attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule is called *hydrogen bond*.
- **Intermolecular hydrogen bonding** is formed between the two different molecules of the same or different compounds *e.g.*, in case of HF, *R*OH or H_2O, etc.
- **Intramolecular hydrogen bonding** is formed between hydrogen atom and an electronegative atom (F, O or N) within the same molecule *e.g.*, in *o*-nitrophenol.
  - An intramolecular hydrogen bond results in the cyclization of the molecules and prevents their association.

Key Points

- Number of hybrid orbitals = Number of atoms bonded to central atom + $\frac{1}{2}$ [Group number of central atom – Valency of the central atom]
- Bond order = $\frac{1}{2}$ [No. of bonding electrons – No. of antibonding electrons]
- Bond order $\propto$ Bond energy $\propto \dfrac{1}{\text{Bond length}}$
- Molecules with bond order equal to zero, do not exist.
- Species with unpaired electrons are paramagnetic and those with all electrons paired are diamagnetic.

Questions for Practice

1. 10 g of a mixture of $CaCO_3$ and $MgCO_3$ has 37.5% $MgCO_3$. What amount of CO_2 is produced at STP when the mixture is strongly heated?
   (a) 1.3 L (b) 2.4 L
   (c) 0.9 L (d) 4.6 L

2. The limiting line in Balmer series will have a frequency of
   (a) $6.22 \times 10^{15}\ s^{-1}$ (b) $7.22 \times 10^{14}\ s^{-1}$
   (c) $8.22 \times 10^{14}\ s^{-1}$ (d) $9.22 \times 10^{14}\ s^{-1}$

3. At a certain temperature and pressure, a 500 mL flask contains 25 mole of nitrogen gas. A different flask at the same temperature and pressure contains 100 mL of helium gas. How many moles of helium are in the second flask?
   (a) 125 (b) 20
   (c) 5 (d) 200

4. When the temperature is raised, the viscosity of the liquid decreases. This is because of
   (a) decreased volume of the solution
   (b) increase in temperature increases the average kinetic energy of molecules which overcome the attractive force between them
   (c) decreased covalent and hydrogen bond forces
   (d) increased attraction between the molecules.

5. Consider the following sets of quantum numbers:

	n	l	m	s
(i)	3	0	0	+1/2
(ii)	2	2	1	+1/2
(iii)	4	3	−2	−1/2
(iv)	1	0	−1	−1/2
(v)	3	2	3	+1/2

   Which of the following sets of quantum numbers is not possible?
   (a) (i), (ii), (iii) and (iv)
   (b) (ii), (iv) and (v)
   (c) (i) and (iii)
   (d) (ii), (iii) and (iv)

6. In a normal spinel type structure, the oxide ions are arranged in *ccp*, whereas, 1/8 tetrahedral holes are occupied by Zn^{2+} ions and 50% of octahedral holes are occupied by Fe^{3+} ions. The formula of the compound is
   (a) $Zn_2Fe_2O_4$ (b) $ZnFe_2O_3$
   (c) $ZnFe_2O_4$ (d) $ZnFe_2O_2$

7. If the radius of first orbit of H-atom is a_0, then de-Broglie wavelength of electron in 4th orbit is
   (a) $2\pi a_0$ (b) $16a_0$
   (c) $a_0/4$ (d) $8\pi a_0$

8. At 27°C, 500 mL of helium gas diffuses in 30 minutes. What is the time (in hours) taken for 1000 mL of SO_2 to diffuse under same experimental conditions?
   (a) 240 (b) 3
   (c) 2 (d) 4

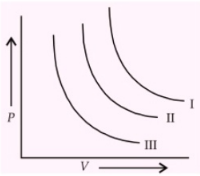
9. With increase of temperature, which of these changes?
   (a) Molality
   (b) Weight fraction of solute
   (c) Fraction of solute present in water
   (d) Mole fraction

10. Zinc oxide is white when cold but yellow when hot because it develops
    (a) Frenkel defect
    (b) Schottky defect
    (c) metal excess defect
    (d) metal deficiency defect.

11. 2 g of a mixture of CO and CO_2 on reaction with excess I_2O_5 produced 2.54 g of I_2. What would be the mass % of CO_2 in the original mixture?
    (a) 60 (b) 30
    (c) 70 (d) 35

12. The ionization enthalpy of hydrogen atom is $1.312 \times 10^6\ J\ mol^{-1}$. The energy required to excite the electron in the atom from $n = 1$ to $n = 2$ is
    (a) $9.84 \times 10^5\ J\ mol^{-1}$ (b) $8.51 \times 10^5\ J\ mol^{-1}$
    (c) $6.56 \times 10^5\ J\ mol^{-1}$ (d) $7.56 \times 10^5\ J\ mol^{-1}$

13. I, II, III are three isotherms respectively at T_1, T_2 and T_3. Temperature will be in order



(a) $T_1 = T_2 = T_3$ (b) $T_1 < T_2 < T_3$
(c) $T_1 > T_2 > T_3$ (d) $T_1 > T_2 = T_3$

14. Compressibility factor for H_2 behaving as real gas is
(a) 1 (b) $\left(1 - \frac{a}{RTV}\right)$
(c) $\left(1 + \frac{Pb}{RT}\right)$ (d) $\frac{RTV}{(1-a)}$

15. Among the following ions, the $p\pi$ and $d\pi$ overlap will be present in
(a) NO_3^- (b) SO_3^{2-}
(c) CO_3^{2-} (d) NO_2^-

16. Match the following.

List I		List II	
A.	1 Faraday	(i)	10^{-5} N
B.	1 Dyne	(ii)	0.2390 cal
C.	1 Joule	(iii)	2.389×10^{-8} cal
D.	1 Litre	(iv)	9.6487×10^4 coulomb
E.	1 Erg	(v)	10^{-3} m^3

(a) A-(iv), B-(i), (C)-(ii), (D)-(v), (E)-(iii)
(b) A-(ii), B-(i), (C)-(iv), (D)-(iii), (E)-(v)
(c) A-(i), B-(ii), (C)-(iii), (D)-(iv), (E)-(v)
(d) A-(v), B-(iii), (C)-(iv), (D)-(ii), (E)-(i)

17. Calculate the ionic radius of a Cs^+ ion assuming the cell edge length for CsCl is 0.4123 nm and that the ionic radius of a Cl^- ion is 0.181 nm.
(a) 0.176 nm (b) 0.231 nm
(c) 0.358 nm (d) 0.116 nm

18. The root mean square speed of oxygen at 27°C is 760 cm s^{-1}. The root mean square speed of hydrogen at the same temperature will be
(a) 3040 cm s^{-1} (b) 190 cm s^{-1}
(c) 1520 cm s^{-1} (d) 760 cm s^{-1}

19. Surface tension of water at 25°C is 7.2×10^{-2} N m^{-1}. In order to increase surface area of water by 100 cm^2, the amount of work done will be
(a) 7.2×10^{-4} J (b) 7.2 J
(c) 72 J (d) 0.72 J

20. Using MO theory predict which of the following species has the shortest bond length.
(a) O_2^{2+} (b) O_2^+
(c) O_2^- (d) O_2^{2-}

21. Two students X and Y report the weight of the same substance as 4.0 g and 4.00 g respectively. Which of the following statements is correct?
(a) Both are equally accurate.
(b) X is more accurate than Y.
(c) Y is more accurate than X.
(d) Both are inaccurate scientifically.

22. Time taken for an electron to complete one revolution in the Bohr orbit of hydrogen atom is
(a) $\frac{4\pi^2 mr^2}{nh}$ (b) $\frac{nh}{4\pi^2 mr}$
(c) $\frac{2\pi mr}{n^2 h^2}$ (d) $\frac{nh}{4\pi^2 mr^2}$

23. The equivalent weight of phosphoric acid H_3PO_4 in the reaction,
$NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$ is
(a) 59 (b) 49
(c) 25 (d) 98

24. Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius)
(a) $\frac{20}{3}\pi r^3$ (b) $\frac{24}{3}\pi r^3$
(c) $\frac{12}{3}\pi r^3$ (d) $\frac{16}{3}\pi r^3$

25. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}?

(a) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$
(b) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(c) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
(d) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

26. In the reaction,
$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 6Cl^-_{(aq)} + 3H_{2(g)}$
(a) 112 L $H_{2(g)}$ at STP is produced for every mole $HCl_{(aq)}$ consumed
(b) 6 L $HCl_{(aq)}$ is consumed for every 3 L $H_{2(g)}$ produced
(c) 33.6 L $H_{2(g)}$ is produced regardless of temperature and pressure for every mole Al that reacts
(d) 67.2 L $H_{2(g)}$ at STP is produced for every mole Al that reacts.

27. Percentages of free space in cubic close packed structure and in body centred packed structure are respectively
(a) 48% and 26%
(b) 30% and 26%
(c) 26% and 32%
(d) 32% and 48%

28. Two separate bulbs contain ideal gases A and B. The density of A is twice as that of gas B. The molecular mass of gas A is half as that of gas B. If two gases are at same temperature, the ratio of the pressures of gas A to that of gas B is
(a) 2
(b) 1/2
(c) 4
(d) 1/4

29. The total number of orbitals in a shell with principal quantum number n is
(a) $2n$
(b) $2n^2$
(c) n^2
(d) $n + 1$

30. Which one of the following pairs of species have the same bond order?
(a) NO^+ and CN^+
(b) CN^- and NO^+
(c) CN^- and CN^+
(d) O_2^- and CN^-

SOLUTIONS

1. **(b)** : Both the carbonates decompose.
$MgCO_3$ is 37.5 % of 10 g = 3.75 g
$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$
84 g — 22.4 L
3.75 g — V_1
$$\frac{84}{3.75} = \frac{22.4}{V_1}$$
$V_1 = 1$ L
$CaCO_3$ is (10 – 3.75) = 6.25 g
$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
100 g — 22.4 L
6.25 g — V_2
$$\frac{100}{6.25} = \frac{22.4}{V_2}$$
$V_2 = 1.4$ L
$V = V_1 + V_2 = 2.4$ L

2. **(c)** : The limiting line of Balmer series refers to the transition of electron from ∞ to 2nd orbit
$\upsilon = c.\bar{\nu}$
$$= 3\times10^{10}\times109677\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\ (\because n_1 = 2, n_2 = \infty)$$
$$= 3.29\times10^{15}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\text{ sec}^{-1}$$
$= 8.22 \times 10^{14}$ sec^{-1}

3. **(c)** : $V_1 = 0.500$ L $V_2 = 0.100$ L
$n_1 = 25$ mole $n_2 = ?$
$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$
$$n_2 = \frac{V_2 n_1}{V_1} = \frac{0.100\times25}{0.500} = 5 \text{ mol}$$

4. **(b)**: With increase in temperature, viscosity of liquid decreases as the average kinetic energy of the molecules increases which overcomes the attractive forces and hence the molecules can move more freely.

5. **(b)** : (i) represents an electron in 3s orbital.
(ii) is not possible as value of l must vary from 0, 1, ... (n – 1).
(iii) represents an electron in 4f orbital.
(iv) is not possible as value of m varies from – l ... +l.
(v) is not possible as value of m varies from –l ... +l, it can never be greater than l.

6. **(c)** : Number of O-atoms per unit cell
$$= \frac{1}{8}\times8+\frac{1}{2}\times6 = 4$$
Number of octahedral holes per unit cell
= 1 × 4 = 4
Number of Fe^{3+} ions per unit cell = $\frac{50\times4}{100} = 2$

Number of tetrahedral voids per unit cell
$= 2 \times 4 = 8$
Number of Zn^{2+} ions per unit cell $= \frac{1}{8} \times 8 = 1$
Hence, formula is $ZnFe_2O_4$.

7. (d) : $r_n = a_0 \times n^2$, $\quad r_4 = a_0 \times 4^2 = 16a_0$

$$mv = 4 \times \frac{h}{2\pi r_4} = \frac{4h}{2\pi \times 16a_0} = \frac{h}{8\pi a_0}$$

$$\therefore \lambda = \frac{h}{mv} = 8\pi a_0$$

8. (d): $\dfrac{r_1}{r_2} = \sqrt{\dfrac{M_2}{M_1}}$

$$\frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\Rightarrow \frac{V_1}{t_1} \times \frac{t_2}{V_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{V_{He}}{t_{He}} \times \frac{t_{SO_2}}{V_{SO_2}} = \sqrt{\frac{M_{SO_2}}{M_{He}}}$$

$$\frac{500}{30} \times \frac{t_{SO_2}}{1000} = \sqrt{\frac{64}{4}}$$

$\therefore$ $t_{SO_2} = 240$ min or 4 hours

9. (c) : Volume increases with rise in temperature.

10. (c) : ZnO when heated shows metal excess defect. Due to the presence of electrons in interstitial sites, it shows colour.

11. (b) : $5CO + I_2O_5 \longrightarrow 5CO_2 + I_2$
1 mole of $I_2 \equiv$ 1 mole of $I_2O_5 \equiv$ 5 mole of CO

Hence, mol of CO $= 5 \times \dfrac{2.54}{254} = 0.05$

Mass of CO $= 0.05 \times 28 = 1.4$ g
Mass of $CO_2 = 2 - 1.4 = 0.6$ g
Mass % of $CO_2 = \dfrac{0.6}{2} \times 100 = 30$

12. (a): $E_1 = -1.312 \times 10^6$ J mol^{-1}

$$E_2 = \frac{E_1}{2^2} = -\frac{1.312 \times 10^6}{4} \text{ J mol}^{-1}$$

$$\Delta E = (E_2 - E_1) = 1.312 \times 10^6 \left(1 - \frac{1}{4}\right)$$

$$= \frac{3}{4} \times 1.312 \times 10^6 = 9.84 \times 10^5 \text{ J mol}^{-1}$$

13. (c): Draw a line at constant pressure parallel to volume-axis. Take volume corresponding to each temperature.
From volume axis, $V_1 > V_2 > V_3$
Hence $T_1 > T_2 > T_3$.

14. (c): For H_2, attractive forces are neglected, due to its small size.

$$\frac{a}{V^2} = 0$$

$$\therefore P(V - b) = RT \quad \Rightarrow \quad PV = RT + Pb$$

$$\therefore \frac{PV}{RT} = \left(1 + \frac{Pb}{RT}\right) = Z$$

15. (b) : Only S atom having *d*-orbitals can undergo $p\pi$-$d\pi$ overlap.

16. (a)

17. (a): CsCl has bcc structure and for it

$$r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3} \times a}{2} = \frac{\sqrt{3} \times 0.4123}{2}$$
$$= \frac{0.7141}{2} = 0.3571 \text{ nm}$$

Now the ionic radius of Cs^+
$r_{Cs^+} + 0.181 = 0.3571$
$r_{Cs^+} + 0.3571 - 0.181 = 0.176$ nm

18. (a): $u = \sqrt{\dfrac{3RT}{M}}$

At the same temperature, $\dfrac{u_1}{u_2} = \sqrt{\dfrac{M_2}{M_1}}$

or $\dfrac{760}{u_2} = \sqrt{\dfrac{2}{32}}$ or $u_2 = 760 \times 4 = 3040$ cm s^{-1}

19. (a) : Work done = surface energy × increase in surface area
$= (7.2 \times 10^{-2} \text{ N m}^{-1}) \times (100 \times 10^{-4} \text{ m}^2) = 7.2 \times 10^{-4}$ J

20. (a): According to MOT, the molecular orbital electronic configuration of

$O_2^{2+} : (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2 = (\pi 2p_y)^2$

$$\therefore \text{ B.O.} = \frac{10 - 4}{2} = 3$$

$O_2^+ : (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\pi^* 2p_x)^1$

$$\therefore \text{ B.O.} = \frac{10 - 5}{2} = 2.5$$

$O_2^-: (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2$
$= (\pi 2p_y)^2(\pi^* 2p_x)^2 = (\pi^* 2p_y)^1$

$\therefore$ B.O. $= \frac{10-7}{2} = 1.5$

$O_2^{2-}: (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2$
$= (\pi 2p_y)^2(\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$

$\therefore$ B.O. $= \frac{10-8}{2} = 1.0$

$\because$ B.O. $\propto \frac{1}{\text{Bond length}}$,

$\therefore$ O_2^{2+} has the shortest bond length.

21. **(c)**: 4.00 is more accurate than 4.0 because the former has three significant figures while the latter has two.

22. **(a)**: By Bohr postulate,

$mvr = n\frac{h}{2\pi}$ or $v = \frac{nh}{2\pi mr}$

No. of revolutions per sec

$$= \frac{\text{Velocity}}{\text{Circumference of the orbit}} = \frac{v}{2\pi r}$$

Substituting value of v, we get

$$= \frac{nh}{2\pi mr} \times \frac{1}{2\pi r} = \frac{nh}{4\pi^2 mr^2}$$

$\frac{nh}{4\pi^2 mr^2}$ revolutions completed in 1s

$\therefore$ 1 revolution will take $\frac{1}{\frac{nh}{4\pi^2 mr^2}} = \frac{4\pi^2 mr^2}{nh}$

23. **(d)**: Only one hydrogen of H_3PO_4 is replaced, *i.e.*, its basicity = 1

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{\text{Basicity}} = \frac{98}{1} = 98$$

24. **(d)** : In case of a face-centred cubic structure, since four atoms are present in a unit cell, hence volume

$$V = 4\left(\frac{4}{3}\pi r^3\right) = \frac{16}{3}\pi r^3$$

25. **(d)** : High charge and small size of the cations increases polarisation.

As the size of the given cations decreases as

$K^+ > Ca^{2+} > Mg^{2+} > Be^{2+}$

Hence, polarising power increases as

$K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

26. **(c)** : $2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 6Cl^-_{(aq)} + 3H_{2(g)}$

At STP, 6 moles of HCl produces 3 moles of H_2 or 3×22.4 lit of HCl

$\therefore$ 1 mole of HCl produces

$\frac{3 \times 22.4}{6} = 11.2$ lit of HCl

Again at STP, 2 moles of Al produces 3 moles of H_2

or 3×22.4 lit of HCl

or 1 mole of Al produces $\frac{3 \times 22.4}{2}$

$= 33.6$ lit of HCl

27. **(c)**: The packing efficiency in a *ccp* structure = 74%

$\therefore$ Percentage free space = 100 – 74 = 26%

Packing efficiency in a body centred structure = 68%

$\therefore$ Percentage free space = 100 – 68 = 32%

28. **(c)**: Given, $d_A = 2d_B$

$M_A = 1/2 M_B$

We know that, $PV = \frac{m}{M}RT \Rightarrow P = \frac{d}{M}RT$

$\because \frac{P_A M_A}{d_A} = \frac{P_B M_B}{d_B}$,

$$\frac{P_A \times 1/2 M_B}{2d_B} = \frac{P_B \times M_B}{d_B} \Rightarrow \frac{P_A}{P_B} = \frac{4}{1}$$

29. **(c)**: Number of orbitals in a shell = n^2

30. **(b)** : In the given pair of species number of electrons in NO^+ = number of electrons in CN^- = 14 electrons.

So they are isoelectronic in nature.

Hence bond order of these two species will also be similar, which is shown here.

$NO^+ \rightarrow (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2$

Bond order = $1/2\,(N_b - N_a) = 1/2\,(10 - 4) = 3$

$CN^- \rightarrow (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2 (\sigma 2p_z)^2$

Bond order $= 1/2\,(10 - 4) = 3$

SOLVED PAPER 2014

Kerala PMT

1. The ratio of de Broglie wavelengths of a deuterium atom to that of an α-particle, when the velocity of the former is five times greater than that of the later, is
   (a) 4 (b) 0.2 (c) 2 (d) 0.4
   (e) 5

2. The maximum number of electrons which can be held by subshell with azimuthal quantum number 'l' in an atom is given by
   (a) $(2l + 1)$ (b) $(2l + 2)$
   (c) $2(2l + 1)$ (d) $2(2l + 2)$
   (e) $2l$

3. Which one of the following data has only four significant figures?
   (a) 6.023×10^{23} (b) 285 cm
   (c) 0.0025 L (d) 0.200 g
   (e) 1.0×10^{5} m

4. The uncertainty in the velocity of a particle of mass 6.626×10^{-31} kg is 1×10^{6} m s^{-1}. What is the uncertainty in its position (in nm)? ($h = 6.626 \times 10^{-34}$ J s)
   (a) $\left(\frac{1}{2\pi}\right)$ (b) $\left(\frac{2.5}{\pi}\right)$
   (c) $\left(\frac{4}{\pi}\right)$ (d) $\left(\frac{1}{4\pi}\right)$
   (e) $\left(\frac{5}{\pi}\right)$

5. The bond orders for O_2^+ and C_2 respectively are
   (a) 2.5, 2 (b) 3, 2
   (c) 2, 2.5 (d) 2, 3
   (e) 3, 3

6. The percentage of s-character in the hybridised orbitals of B in BF_3 is
   (a) 25 (b) 50 (c) 75 (d) 33.3
   (e) 21.5

7. Which one of the following has the lowest dipole moment?
   (a) CH_3F (b) CH_3Cl
   (c) CH_3I (d) $CHCl_3$
   (e) CH_3Br

8. The number of bond pair and lone pair of electrons respectively in NH_3 molecule are
   (a) 4 and 0 (b) 3 and 0
   (c) 3 and 1 (d) 2 and 2
   (e) 5 and 0

9. The partial pressure of nitrogen in air is 0.76 atm. and its Henry's law constant is 7.6×10^{4} atm at 300 K. What is the mole fraction of N_2 in the solution obtained when air is bubbled through water at 300 K?
   (a) 1×10^{-4} (b) 2×10^{-4}
   (c) 1×10^{-5} (d) 2×10^{-5}
   (e) 1×10^{-6}

10. The type of attractive forces that operate between gaseous HCl and chlorine molecule is
    (a) dipole-dipole forces
    (b) London forces
    (c) induced dipole-induced dipole
    (d) dipole- induced dipole forces
    (e) electrostatic forces.

11. Which one of the following statements is incorrect?
    (a) Glass is an extremely viscous liquid.
    (b) Viscosity co-efficient of a liquid decreases with increase in temperature.
    (c) Laminar flow represents regular gradation of velocity in passing from one layer to another in liquids.

(d) Liquids rise in capillary due to surface tension.
(e) Gases can be liquefied at any temperature by applying sufficient pressure.

12. The number of tetrahedral and octahedral voids in a *ccp* array of 100 atoms are respectively
(a) 200 and 100 (b) 100 and 200
(c) 200 and 200 (d) 100 and 100
(e) 50 and 50

13. Which of the following pairs contain metalloid elements in the periodic table?
(a) Na and K (b) F and Cl
(c) Ca and Mg (d) As and Si
(e) Cu and Ag

14. The atom/ion that has the highest number of unpaired electrons is
(a) Na^+ (b) F (c) N (d) O^{2-}
(e) B

15. The inorganic compound obtained by the auto-oxidation of 2-alkylanthraquinol is
(a) H_2O (b) H_2O_2 (c) H_2 (d) O_2
(e) H_2SO_4

16. The least stable carbonate of alkali metals is
(a) Cs_2CO_3 (b) Na_2CO_3
(c) K_2CO_3 (d) Rb_2CO_3
(e) Li_2CO_3

17. Sphalerite is concentrated by
(a) gravity separation
(b) froth floatation
(c) magnetic separation
(d) hydraulic washing
(e) leaching.

18. The following set of reactions are used in refining zirconium.

$$Zr(impure) + 2I_2 \xrightarrow{523\ K} ZrI_4 \xrightarrow{1800\ K} Zr(pure) + 2I_2$$

This method is known as
(a) distillation (b) liquation
(c) Hall-Heroult method
(d) van Arkel method
(e) Mond's process.

19. Which one of the following is used as a piezoelectric material?
(a) Silicones (b) Graphite
(c) Silica gel (d) Kieselghur
(e) Quartz.

20. The gaseous product formed when HOCl reacts with H_2O_2 in acidic medium is
(a) H_2 (b) Cl_2 (c) O_2 (d) $HClO_2$
(e) $HClO_3$

21. Three centre two electron bond is present in
(a) NH_3 (b) B_2H_6 (c) BCl_3 (d) $AlCl_3$
(e) BF_3

22. Which one of the following is used for the production of UF_6 in the enrichment of U^{235}?
(a) ClF_3 (b) KF (c) KHF_2 (d) HF
(e) PF_3

23. Ziegler-Natta catalyst is
(a) $ZnCl_2$ (b) $Et_3Al + TiCl_4$
(c) $Cu/ZnO–Cr_2O_3$ (d) Pt
(e) V_2O_5

24. Among the 3*d*-series of transition metals the one that has positive M^{2+}/M standard electrode potential is
(a) Cr (b) Mn (c) Zn (d) Ni
(e) Cu

25. Which one of the following transition metal ions is colourless in aqueous solution?
(a) Ti^{4+} (b) V^{4+} (c) Mn^{2+} (d) Fe^{3+}
(e) Ni^{2+}

26. The magnetic moment of Ni^{2+} ion (At. no. of Ni is 28) in B.M. unit is
(a) 1.73 (b) 4.81 (c) 5.96 (d) 2.84
(e) 3.86

27. The enthalpy of formation of $CH_{4(g)}$, $H_2O_{(l)}$ and $CO_{2(g)}$ are respectively – 74.8 kJ mol^{-1}, –285.8 kJ mol^{-1} and –393.5 kJ mol^{-1}. Then, the standard enthalpy of combustion of $CH_{4(g)}$ is
(a) +890.3 kJ mol^{-1} (b) – 604.5 kJ mol^{-1}
(c) –754.1 kJ mol^{-1} (d) +604.5 kJ mol^{-1}
(e) – 890.3 kJ mol^{-1}

28. In the following reaction,
$4NO_{2(g)} + O_{2(g)} \longrightarrow 2N_2O_{5(g)}$; $\Delta H = -110$ kJ; if $N_2O_{5(s)}$ is formed instead of $N_2O_{5(g)}$ in the reaction, the enthalpy change (in kJ) would be (enthalpy of sublimation of $N_2O_{5(s)}$ is + 53 kJ mol^{-1})
(a) –216 (b) –162 (c) +108 (d) +216
(e) +162

29. For the reaction $2A_3 \rightleftharpoons 3A_2$ the equilibrium constant and the ΔG° values at a certain temperature are respectively 1×10^{30} and -172.4 kJ mol^{-1}. The equilibrium temperature in °C is about ($2.303\ R = 19.15$ J K^{-1} mol^{-1})
(a) 300 (b) 27 (c) 273 (d) 298
(e) 270

30. The equilibrium constant (K_c) for the reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ at 800 K is 0.0625. What is the K_c value for the following reaction at 800 K?

$$NO_{(g)} \rightleftharpoons \frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)}$$

(a) 0.4 (b) 0.375 (c) 4 (d) 40
(e) 0.20

31. When ammonium chloride is added to ammonium hydroxide solution, the dissociation of ammonium hydroxide is suppressed due to
(a) hydrolysis
(b) oxidation
(c) reduction
(d) increase in dielectric constant
(e) common ion effect.

32. The pK_a of a weak acid HA and pK_b of a weak base BOH are 4.60 and 4.80 respectively. The pH of 0.1 M solution of the salt, BA, formed from the acid HA and base BOH is
(a) 7.10 (b) 9.40 (c) 6.90 (d) 0.20
(e) 4.80

33. In which one of the following equilibria will the point of equilibrium shift to left when the pressure of the system is increased?
(a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
(b) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$
(c) $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$
(d) $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$
(e) $2H_{2(g)} + O_{2(g)} \rightleftharpoons H_2O_{(l)}$

34. The experimental and calculated elevation in boiling points of an electrolyte AB in its aqueous solution at a given concentration are 0.81 K and 0.54 K respectively. The percentage ionization of the electrolyte at this concentration is
(a) 20 (b) 40 (c) 50 (d) 60
(e) 80

35. Which one of the following binary liquid mixtures exhibits negative deviation from Raoult's law?
(a) n-Hexane – n-Heptane
(b) Chloroform – Acetone
(c) Carbon disulphide–Acetone
(d) Bromoethane – Chloroethene
(e) Benzene–Toluene

36. An electrolyte (AB) is 100% ionized in 10% aqueous solution. What is the osmotic pressure (L-atm) of a 10% solution of the electrolyte at 300 K, if molecular weight of AB is 200 g mol^{-1}? ($R = 0.082$ L atm K^{-1} mol^{-1})
(a) 200 (b) 100 (c) 246 (d) 24.6
(e) 2.46

37. In the electrolysis of aqueous solution of copper sulphate using copper strips as anode and cathode, the anode reaction is
(a) $Cu^{2+} + 2e^- \longrightarrow Cu$
(b) $Cu \longrightarrow Cu^{2+} + 2e^-$
(c) $2HO^- \longrightarrow H_2 + \frac{1}{2}O_2 + 2e^-$
(d) $SO_4^{2-} \longrightarrow SO_4 + 2e^-$
(e) $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$

38. 0.001 mole of strong electrolyte $Zn(OH)_2$ is present in 200 mL of an aqueous solution. The pH of this solution is
(a) 2 (b) 4 (c) 12 (d) 10
(e) 7

39. If the standard potential for Daniell cell is 1.1 V, then the potential of the cell when $[Zn^{2+}] = 1.0$ M and $[Cu^{2+}] = 0.1$ M at 298 K is

$$\left(\frac{2.303\ RT}{F} \text{ value at 298 K} = 0.06 \text{ V}\right)$$

(a) 1.1295 V (b) 0.100 V
(c) 1.07 V (d) 0.76 V
(e) 1.1 V

40. The $t_{1/2}$ for a zero order reaction at the initial concentration of 6×10^{-3} M is one minute at 27 °C. The rate constant at 27 °C in mol dm^{-3}s^{-1} is
(a) 3×10^{-4} (b) 6×10^{-4}
(c) 5×10^{-5} (d) 5×10^{-4}
(e) 3×10^{-5}

41. The inversion of cane sugar is first order in [sugar] and proceeds with half-life of 600 minutes at pH = 4 for a given concentration of sugar. However, if pH = 5, the half-life changes to 60 minutes. The rate law expression for the sugar inversion can be written as

(a) rate = $k[\text{sugar}]^1[H^+]^2$

(b) rate = $k[\text{sugar}]^1[H^+]^1$

(c) rate = $k[\text{sugar}]^1H^+]^4$

(d) rate = $k[\text{sugar}]^1[H^+]^0$

(e) rate = $k[\text{sugar}]^1[H^+]^5$

42. In an attempt to compare the half-lives of two radioactive elements *A* and *B*, a scientist set aside 400 g of each. After 3 months, the scientist found 25 g of *A* and 200 g of *B*. Which one of the following statements is true?

(a) Half-life of *B* is twice that of *A*.
(b) Half-life of *B* is four times that of *A*.
(c) Half-life of *A* is twice that of *B*.
(d) Half-life of *A* is four times that of *B*.
(e) Half-life of *B* is eight times that of *A*.

43. When molten magnesium oxide was electrolysed for a certain period, 150 mg of Mg was deposited on the cathode. The volume of oxygen gas in cm^3 at STP conditions liberated at the anode during the same period is (Atomic mass of Mg = 24 g mol^{-1})

(a) 140 (b) 280 (c) 70 (d) 120
(e) 240

44. Which one of the following is not explained by adsorption?

(a) When acetic acid solution is shaken with charcoal, the concentration of the acid decreases.
(b) The white precipitate of $Mg(OH)_2$ attains blue colour when precipitated in the presence of magneson reagent.
(c) The air becomes dry in the presence of silica gel.
(d) An aqueous solution of NaOH attains pink colour with a drop of phenolphthalein.
(e) When animal charcoal is shaken with coloured methylene blue solution, the solution turns colourless.

45. The hybridization of central metal ion in $K_2[Ni(CN)_4]$ and $K_2[NiCl_4]$ are respectively

(a) dsp^2, sp^3 (b) sp^3, sp^3
(c) dsp^2, dsp^2 (d) sp^3, sp^3d^2
(e) sp^3d^2, d^2sp^3

46. Which of the following compounds show optical isomerism?

(i) *Cis*-$[Co(NH_3)_4Cl_2]^+$
(ii) *Trans*-$[Co(en)_2Cl_2]^+$
(iii) *Cis*-$[Co(en)_2Cl_2]^+$
(iv) $[Co(en)_3]^{3+}$

Choose the correct answer codes given below.

(a) (i) and (ii) (b) (ii) and (iii)
(c) (iii) and (iv) (d) (i), (iii) and (iv)
(e) (i), (ii), (iii) and (iv).

47. Camphor can be purified by

(a) distillation
(b) vacuum distillation
(c) sublimation
(d) steam distillation
(e) fractional crystallization.

48. Tropolone is an example of

(a) benzenoid aromatic compound
(b) non-benzenoid aromatic compound
(c) alicyclic compound
(d) acyclic compound
(e) heterocyclic aromatic compound.

49. Both sp^2 and sp^3 hybrid orbitals are involved in the formation of

(a) $CH_2{=}CH{-}C{\equiv}C{-}H$
(b) $CH_3{-}CH_2{-}CH_2{-}CH_3$
(c) $CH_2{=}CH{-}C{\equiv}N$
(d) $CH_2{=}CH_2$
(e) $CH_2{=}CH{-}CO{-}CH_3$

50. Arrange the following molecules in the correct order of decreasing C—C bond length :

$$C_2H_6, C_2H_4, C_2H_2, C_6H_6$$

(a) $C_2H_6 > C_6H_6 > C_2H_4 > C_2H_2$
(b) $C_2H_6 > C_2H_4 > C_6H_6 > C_2H_2$
(c) $C_2H_4 > C_2H_2 > C_2H_6 > C_6H_6$
(d) $C_2H_2 > C_6H_6 > C_2H_4 > C_2H_6$
(e) $C_6H_6 > C_2H_4 > C_2H_6 > C_2H_2$

51. Williamson's synthesis of preparing dimethyl ether is a/an
(a) electrophilic substitution
(b) S_N1 reaction
(c) electrophilic addition
(d) S_N2 reaction
(e) free radical substitution.

52. The effect that makes 2, 3-dimethy1-2-butene more stable than 2-butene is
(a) resonance (b) hyperconjugation
(c) electromeric effect
(d) inductive effect (e) steric effect.

53. In which of the following compounds only primary carbon atoms are present?
(a) $CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3$
(b) $CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$
(c) $CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$ (d) $CH_3-CH_2-CH_3$
(e) CH_3-CH_3

54. The organic compound with two asymmetric carbon atoms is
(a) 3, 4-dimethylheptane
(b) 3-methyl-1-pentene
(c) 2-chloropentane
(d) 5-ethyl-2, 3-dimethylheptane
(e) 3-chlorohexane.

55. Geometrical isomerism is not possible in
(a) 2, 4-hexadiene (b) benzaldoxime
(c) but-2-ene
(d) 1, 2-dichloroethene
(e) benzophenone oxime.

56. The correct IUPAC name of the organic compound $CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2OH$ is
(a) 4-chloro-2,3-dimethylpentan-1-o1
(b) 2-chloro-3, 4-dimethylpentan-5-o1
(c) 2, 3-dimethyl-4-chloropentan-1-o1
(d) 2-chloro-3, 4-dimethyl *n*-pentyl alcohol
(e) 2, 3-dimethyl-4-chloro *n*-pentyl alcohol.

57. Carbylamine test is not answered by
(a) $C_6H_5NH_2$
(b) $(CH_3)_3C-CH_2-NH_2$
(c) $C_6H_5CH_2NH_2$
(d) $(CH_3)_3N$ (e) CH_3NH_2

58. Which of the following represents Wurtz-Fittig reaction?
(a) $C_6H_5I + 2Na + CH_3I \longrightarrow C_6H_5CH_3 + 2NaI$
(b) $2C_6H_5I + 2Na \longrightarrow C_6H_5C_6H_5 + 2NaI$
(c) $2CH_3CH_2I + 2Na \longrightarrow CH_3CH_2CH_2CH_3 + 2NaI$
(d) $C_2H_5ONa + C_2H_5I \longrightarrow C_2H_5-O-C_2H_5 + NaI$
(e) $CH_3Br + AgF \longrightarrow CH_3F + AgBr$

59. Which of the following organic halogen compounds undergoes hydrolysis with aqueous NaOH predominantly by S_N1 mechanism?
(a) Ethyl iodide (b) Methyl chloride
(c) Isopropyl chloride (d) Chlorobenzene
(e) Benzyl chloride

60. The major product formed when 2-bromo-2-methylbutane is refluxed with ethanolic KOH is
(a) 2-methylbut-2-ene
(b) 2-methylbutan-1-o1
(c) 3-methylbutan-2-ol
(d) 2-methylbutan-2-ol
(e) 2-methylbut-1-ene.

61. In which of the following reactions new carbon-carbon bond is not formed?
(a) Cannizzaro reaction
(b) Wurtz reaction
(c) Aldol condensation
(d) Friedel-Craft reaction
(e) Kolbe's reaction.

62. Which one of the following phenols has the highest pK_a value?
(a) *o*-Nitrophenol (b) Phenol
(c) *m*-Nitrophenol (d) Picric acid
(e) *p*-Cresol.

63. The reagent that is used to distinguish between secondary amine and tertiary amine is
(a) *p*-toluenesulphonyl chlorides
(b) Lucas reagent
(c) $CHCl_3$ and alc. KOH
(d) Borsche's reagent (e) bromine water.

64. Which one of the following isomeric amines has the highest boiling point?
(a) $CH_3-CH_2-CH_2-NH-CH_3$
(b) $CH_3-CH_2-NH-CH_2-CH_3$
(c) $(CH_3)_2N-CH_2-CH_3$
(d) $CH_3-CH_2-CH_2-CH_2-NH_2$
(e) $(CH_3)_2CH-NH-CH_3$

65. Which one of the following reagent will convert acetamide to ethanamine?
(a) Phosphorus pentoxide
(b) Lithium aluminium hydride
(c) Potassium cyanide
(d) Thionyl chloride
(e) Bromine and sodium hydroxide.

66. Match the following -

	List-I		List-II
A.	Acetaldehyde, Vinyl alcohol	(i)	Enantiomers
B.	Eclipsed and staggered ethane	(ii)	Tautomers
C.	(+)-2-Butanol, (–)-2-Butanol	(iii)	Chain isomers
D.	Methyl-*n*-propyl-amine and Diethylamine	(iv)	Conformational isomers
		(v)	Metamers

(a) (A) → (ii), (B) → (iv), (C) → (iii), (D) → (v)
(b) (A) → (i), (B) → (ii), (C) → (iii), (D) → (iv)
(c) (A) → (v), (B) → (i), (C) → (iv), (D) → (ii)
(d) (A) → (v), (B) → (i), (C) → (iii), (D) → (ii)
(e) (A) → (ii), (B) → (iv), (C) → (i), (D) → (v)

67. Which one of the following is an example for biodegradable polyester?
(a) PHBV (b) PET
(c) Nylon 6 (d) Bakelite
(e) Glyptal.

68. Which one of the following is an essential amino acid?
(a) Methionine (b) Tyrosine
(c) Proline (d) Glycine
(e) Alanine.

69. The one letter code for the amino acid tryptophan is
(a) G (b) V (c) W (d) H
(e) A

70. Cheilosis and digestive disorders are due to the deficiency of
(a) vitamin A (b) thiamine
(c) riboflavin (d) ascorbic acid
(e) pyridoxine.

71. Which one of the following is a bacteriostatic drug?
(a) Aminoglycosides (b) Penicillin-G
(c) Ofloxacin (d) Ampicillin
(e) Tetracycline.

72. Freon-12 is manufactured from tetrachloromethane by
(a) Haloform reaction
(b) Reimer-Tiemann reaction
(c) Wurtz reaction
(d) Swartz reaction
(e) Gattermann reaction.

SOLUTIONS

1. (d) : Using de Broglie's equation,

$$\lambda = \frac{h}{mv};\ \lambda \propto \frac{1}{mv}$$

$$\frac{\lambda_D}{\lambda_\alpha} = \frac{(mv)_\alpha}{(mv)_D} \quad ...(i)$$

On putting the values in equation (i), we get

$$\frac{\lambda_D}{\lambda_\alpha} = \frac{4\times 1}{2\times 5} \Rightarrow 0.4$$

2. (c)

3. (a) : In exponential notation, only the numerical portion gives the number of significant figures. Hence, 6.023×10^{23} has four significant figures.

4. (d) : According to Heisenberg uncertainty principle, $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$

$$\Delta x = \frac{h}{4\pi \cdot m\Delta v} \quad [\because \Delta p = m\Delta v]$$

$$= \frac{6.626\times 10^{-34}}{4\pi \times 6.626\times 10^{-31} \times 1\times 10^{6}}$$

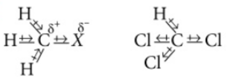
$$= \frac{1\times 10^{-9}}{4\pi} \text{ or } \frac{1}{4\pi} \text{ nm}$$

5. **(a) :** Bond order $= \dfrac{N_b - N_a}{2}$

Species	No. of electrons	M.O. configuration	B.O.
O_2^+	15	$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, (\pi 2p_x^2 = \pi 2p_y^2), (\pi^* 2p_x^1 = \pi^* 2p_y^0)$	2.5
C_2	12	$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, (\pi 2p_x^2 = \pi 2p_y^2)$	2

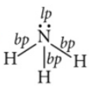
6. **(d):** BF_3 molecule is sp^2-hybridised. Hence, the s-character of B is 33.3%.

7. **(d):**



The C—X(X = F, Cl, Br and I) bond is polar because halogens are more electronegative than carbon. Hence, all the bond moments are in one direction in case of CH_3X but not in $CHCl_3$.

8. **(c) :**

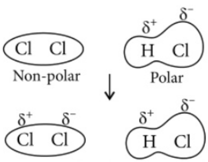


9. **(c) :** According to Henry's law, $p = k_H \cdot x$

$0.76 = 7.6 \times 10^4 \times x$

$$x = \frac{0.76}{7.6 \times 10^4} \Rightarrow 1 \times 10^{-5}$$

10 **(d):** The force of attraction between a polar $HCl_{(g)}$ and a non-polar Cl_2 molecule is dipole-induced dipole forces.



(Electrons get attracted to the positive end of the HCl dipole, inducing a dipole in the Cl_2-molecule.)

11. **(e) :** Gases cannot be liquefied above their critical temperature howsoever, high pressure is applied.

12. **(a) :** In *ccp*,

No. of tetrahedral voids = 2 N

No. of octahedral voids = N

(where N = no. of atoms forming closed packing)

Hence, for 100 atoms, tetrahedral voids = 200 and octahedral voids = 100

13. **(d):** Na and K – Alkali metals

F and Cl – Halogens

Ca and Mg – Alkaline earth metals

As and Si – Metalloids

Cu and Ag – Transition metals

14. **(c) :**

Atoms/ ions	At. no.	No. of electrons	Electronic configu-ration	No. of unpaired electrons
Na^+	11	10	$1s^2\, 2s^2\, 2p^6$	0
F	9	9	$1s^2\, 2s^2\, 2p^5$	1
N	7	7	$1s^2\, 2s^2\, 2p^3$	3
O^{2-}	8	10	$1s^2\, 2s^2\, 2p^6$	0
B	5	5	$1s^2\, 2s^2\, 2p^1$	1

15. **(b)**

16. **(e) :** On heating, Li_2CO_3 readily decomposes into its oxide and CO_2 while the other carbonates are resistant to the heat.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

17. **(b):** The froth floatation process is used to concentrate sulphide ores. Sphalerite is zinc sulphide (ZnS).

18. **(d):** In van Arkel method, the impure metal is converted into volatile compound which is then decomposed electrically to get pure metal.

19. **(e)**

20. **(c) :** H_2O_2 reduces hypohalous acid (HOCl) to halide ion in acidic medium,

$H_2O_2 + HOCl \longrightarrow HCl + H_2O + O_2$

21. **(b):** In diborane (B_2H_6), two B—H—B bridging bonds are formed, each of which consists of two electrons, forming 3*c*-2*e* bonds (*i.e.* 3 atoms share 2 electrons). Because of the shape of the electron cloud formed it is also called 'banana bond'.

22. (a) : ClF_3 is mainly use to produce uranium hexafluoride, UF_6, as a part of nuclear fuel processing and reprocessing.

$U_{(s)} + 3ClF_{3(l)} \longrightarrow UF_{6(g)} + 3ClF_{(g)}$

23. (b) : Ziegler-Natta catalyst is $(C_2H_5)_3Al + TiCl_4$, used for the polymerization of alkenes.

24. (e) : Among the given metals, only copper (below hydrogen) has positive Cu^{2+}/Cu standard electrode potential.

25. (a) :

Ions	Outer configuration	No. of unpaired electrons
Ti^{4+}	$3d^0$	$0 \longrightarrow$ Colourless
V^{4+}	$3d^1$	1 Coloured ions
Mn^{2+}	$3d^5$	5 Coloured ions
Fe^{3+}	$3d^5$	5 Coloured ions
Ni^{2+}	$3d^8$	2 Coloured ions

26. (d) : $Ni^{2+}(28) : [Ar]3d^8 4s^0$

$n = 2$ where n = no. of unpaired electrons

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$
$$= \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ B.M.}$$

27. (e) : $CH_{4(g)} + 2O_{2(g)} \longrightarrow 2H_2O_{(l)} + CO_{2(g)}$

Applying the Hess's law,

$$\Delta H^\circ = 2\Delta H^\circ_{f(H_2O)} + \Delta H^\circ_{f(CO_2)} - \Delta H^\circ_{f(CH_4)}$$
$$= 2 \times (-285.8) + (-393.5) - (-74.8)$$
$$= -571.6 - 393.5 + 74.8 = -890.3 \text{ kJ mol}^{-1}$$

28. (a) :

$$4NO_{2(g)} + O_{2(g)} \longrightarrow 2N_2O_{5(g)};\ \Delta H = -110 \text{ kJ}$$

$$2N_2O_{5(g)} \xrightarrow{-53 \text{ kJ mol}^{-1}} 2N_2O_{5(s)}$$

$$4NO_{2(g)} + O_{2(g)} \xrightarrow{\Delta H' = ?} 2N_2O_{5(s)}$$

Applying the Hess's law,

$$\Delta H' = -110 + 2(-53)$$
$$= -110 - 106 = -216 \text{ kJ}$$

29. (b) : $\Delta G^\circ = -\,2.303\,RT \log K$

$-172.4 = -\,2.303\,RT \log 1 \times 10^{30}$

$-172.4 = -19.15 \times 10^{-3}\,T \log 1 \times 10^{30}$

$-\,172.4 = -\,19.15 \times 10^{-3}\,T\,(\log 1 + 30 \log 10)$

$-172.4 = -19.15 \times 10^{-3} \times 30\,T \log 10$

$[\because \log 1 = 0, \log 10 = 1]$

$$T = \frac{-172.4}{-19.15 \times 10^{-3} \times 30} = 300.08 \text{ K or } 27\,°\text{C}$$

30. (c) : For the reaction, $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

At equilibrium,

$$K_c = \frac{[NO]^2}{[N_2][O_2]} \quad \text{...(i)}$$

For another reaction,

$$NO_{(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)}$$

At equilibrium,

$$K_c' = \frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]} \quad \text{... (ii)}$$

On squaring and reverse the equation (ii), we get

$$\frac{1}{K_c'^2} = \frac{[NO]^2}{[N_2][O_2]} \quad \text{...(iii)}$$

Equating equations (i) and (iii), we get

$$K_c = \frac{1}{K_c'^2} \quad \text{or} \quad K_c' = \frac{1}{\sqrt{K_c}}$$

$$= \frac{1}{\sqrt{0.0625}} = \frac{1}{\sqrt{\dfrac{625}{10000}}} = \frac{1}{\dfrac{25}{100}} = 4$$

31. (e) : The addition of NH_4Cl to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion *i.e.* NH_4^+ in NH_4Cl.

32. (c) : For the salt of weak acid (HA) and weak base (BOH) :

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$$
$$= \frac{1}{2}[14 + 4.60 - 4.80] = \frac{1}{2}[13.8] = 6.90$$

33. (b) : An increase in pressure applied to a system at equilibrium, favours the reaction in the direction that produces smaller no. of gaseous moles. Thus, only in the reaction,

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$$

there are smaller no. of gaseous moles on left hand side.

34. (c) : van't Hoff factor,

$$i = \frac{\text{Observed elevation in b.p.}}{\text{Calculated elevation in b.p.}} = \frac{0.81}{0.54} = 1.5$$

$$\begin{array}{lll} AB & \rightleftharpoons A^+ + & B^- \\ 1-\alpha & \quad \alpha & \alpha \end{array}$$

(where, α = degree of ionization)

Total no. of particles = $1 - \alpha + \alpha + \alpha$
$i = 1 + \alpha$
$1.5 = 1 + \alpha$
$\alpha = 0.5$ *i.e.* 50%

35. (b)

36. (d): $\underset{(1-\alpha)}{AB} \rightleftharpoons \underset{\alpha}{A^+} + \underset{\alpha}{B^-}$

Total no. of particles = $1 - \alpha + \alpha + \alpha$
$i = 1 + \alpha$ (α = degree of ionization)
As electrolyte is 100% ionized *i.e.,* $\alpha = 1$
then $i = 1 + 1 = 2$
$\pi V = i.CRT$

$$\pi = i \times \frac{w}{M} \times \frac{RT}{V}$$

$$\pi = 2 \times \frac{10}{200} \times \frac{0.082 \times 300}{0.1}$$

π = 24.6 L-atm

37. (b): Electrolysis of $CuSO_4$ solution using copper electrodes, $CuSO_4$ ionises as :
$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$; at anode (Oxidation)
$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$; at cathode (Reduction)
The copper dissolves at the anode and is deposited at the cathode.

38. (c) : $Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^-$

$$[OH^-] = 0.001 \times 2 \times \frac{1000}{200}$$

$[OH^-] = 1 \times 10^{-2}$ mol L^{-1}
pOH = $-\log[OH^-] = -\log(1 \times 10^{-2}) = +2 \log 10$
pOH = 2 ; pH + pOH = 14
pH + 2 = 14 ; pH = 12

39. (c) : According to Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{nF}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

In Daniell cell,
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(s)}$

$$E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{nF}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = E^\circ_{cell} + \frac{0.06}{n}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$E_{cell} = 1.1 + \frac{0.06}{2}\log_{10}\frac{(0.1)}{(1.0)}$$

$E_{cell} = 1.1 + 0.03 \log (0.1)$
$E_{cell} = 1.1 + 0.03(-1)$ [$\because \log 0.1 = -1$]
$= 1.07$ V

40. (c) : For a zero order reaction,
$A \longrightarrow$ product, rate = k

$$t_{1/2} = \frac{[A]_0}{2\,k}$$

$$k = \frac{[A]_0}{2 \times t_{1/2}} = \frac{6 \times 10^{-3}}{2 \times 60} = 5 \times 10^{-5}\ \text{mol dm}^{-3}\text{s}^{-1}$$

41. (d): Inversion of cane sugar is a first order reaction.
Sugar + $H_2O \xrightarrow{H^+}$ Glucose + Fructose
and for first order reaction, $t_{1/2}$ is independent of initial concentration.
So, rate = $k[\text{sugar}]^1\,[H^+]^n$ ... (i)
(where, n = order of reaction)

Now, $t_{1/2}$ for $[H^+] \propto \dfrac{1}{[C]_0^{n-1}}$ or $\propto [C]_0^{1-n}$

At pH = 4, $600 \propto [10^{-4}]^{1-n}$ ... (ii)
At pH = 5, $60 \propto [10^{-5}]^{1-n}$ ...(iii)
Dividing equations (ii) and (iii),we get

$$\frac{600}{60} = \left(\frac{10^{-4}}{10^{-5}}\right)^{1-n};\ \frac{10}{1} = (10)^{1-n}$$

$(10)^{1-n} = (10)^1$
$1 - n = 1 \Rightarrow n = 0$
Now, putting the value of n in equation (i), we get
Rate = $k[\text{sugar}]^1[H^+]^0$

42. (b): After 3 months,

$t_{1/2}$=	1	2	3	4
400 g $\longrightarrow$	200 g $\longrightarrow$	100 g $\longrightarrow$	50 g $\longrightarrow$	25 g
[Sample] 'A' or 'B'	'B'			'A'

For element A, 4 Half-lives = 3 months (Faster)
For element B, 1 Half-life = 3 months (Slower)
Hence, half-life of B is 4 times that of A.

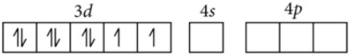
43. (c) : $MgO_{(s)} \longrightarrow Mg_{(s)} + \frac{1}{2} O_{2(g)}$

No. of moles of Mg $= \dfrac{0.15}{24} = 6.25 \times 10^{-3}$

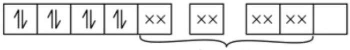
No. of moles of $O_2 = \dfrac{6.25 \times 10^{-3}}{2}$
$= 3.125 \times 10^{-3}$
$\therefore$ Volume of $O_2 = 3.125 \times 10^{-3} \times 22400$
$= 70\ \text{cm}^3$

44. (d): Phenolphthalein indicator changes into pink colour due to change in pH of the solution.

45. (a) : For the complex ion, $[Ni(CN)_4]^{2-}$,
$Ni^{2+}(28) : [Ar]\ 3d^8\ 4s^0$



$[Ni(CN)_4]^{2-}$ ion :



dsp^2 hybridization

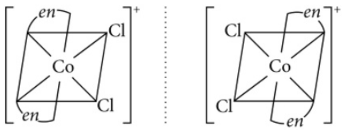
[CN^- is a strong field ligand.]

For $[NiCl_4]^{2-}$ ion ,

sp^3 hybridization

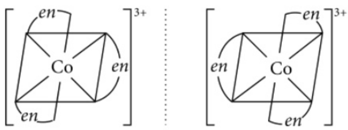
[Cl^- is a weak field ligand.]

46. (c) : Complexes of the type *cis*-$[M(AA)_2B_2]^{n\pm}$ and $[M(AA)_3]^{n\pm}$ show optical isomerism.



cis-d-isomer   mirror   *cis-l*-isomer

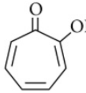
and



(*d*-isomer)   mirror   (*l*-isomer)

47. (c) : Camphor is a sublimable substance. Hence, purified by sublimation process.

48. (b) : Aromatic compounds which do not contain a benzene ring but instead contain other highly unsaturated ring are called non-benzenoid aromatic compounds.



Tropolone

49. (e) : $\underset{sp^2}{CH_2}=\underset{sp^2}{CH}-\underset{sp^2}{\overset{\overset{O}{\|}}{C}}-\underset{sp^3}{CH_3}$

50. (a) : $\xrightarrow{\text{Bond length decreases}}$
$\underset{sp^3}{C-C} > \underset{sp^2}{C=C} > \underset{sp}{C\equiv C}$

Benzene having conjugated system. Hence, its bond length lie between C—C and C$=$C bond. So, the order is
$C_2H_6 > C_6H_6 > C_2H_4 > C_2H_2$

51. (d): Williamson's synthesis is a nucleophilic substitution reaction and proceeds *via* S_N2 mechanism.

52. (b): Larger the no. of methyl groups linked to C$=$C bond, more is the no. of hyperconjugative C — H bonds and greater is the stability of alkene.

$(CH_3)_2C=C(CH_3)_2 > CH_3CH=CHCH_3$

2, 3-Dimethyl-2-butene (12 α- hydrogen atoms)   2-Butene (6 α-hydrogen atoms)

53. (e) : $\overset{1^\circ}{CH_3}-\overset{1^\circ}{CH_3}$

54. (a) : $CH_3-CH_2-CH_2-\underset{\underset{H_3C}{|}}{\overset{\overset{H}{|}}{^*C}}-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{^*C}}-CH_2-CH_3$

55. (e) : $C_6H_5-\underset{\underset{N-OH}{\|}}{C}-C_6H_5$

Benzophenone oxime

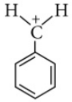
Since carbon atom is achiral *i.e.* contains two similar $-C_6H_5$ groups, hence geometrical isomerism is not possible.

56. (a)

57. (d): Only 1° amine ($R-NH_2$) gives carbylamine test.

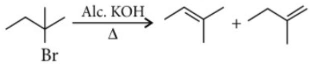
58. (a) : Reaction of alkyl halide and aryl halide with Na in dry ether to form alkyl substituted aromatic compound is known as 'Wurtz-Fittig reaction.'

59. (e) : Benzyl chloride undergoes S_N1 reaction because benzyl carbocation is stabilised by delocalisation of electrons to benzene ring.



Benzyl carbocation

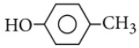
60. (a) : According to Saytzeff's rule, the compound undergoes elimination reaction to form more substituted alkene as the major product.



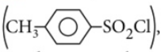
2-Bromo-2-methylbutane — 2-Methylbut-2-ene (70%) — 2-Methylbut-1-ene (30%)

61. (a) : $\underset{\text{Formaldehyde}}{2HCHO} + NaOH \longrightarrow \underset{\text{Sodium formate}}{HCOONa} + \underset{\text{Methyl alcohol}}{CH_3OH}$

No new C—C bond is formed.

62. (e) : 

p-Cresol contains electron donating group ($—CH_3$), which decreases the acidity. Hence, the pK_a value is highest for *p*-cresol.

63. (a) : The *p*-toluene sulphonyl chloride 

, producing the corresponding *p*-toluenesulphonamide. Futher, 2°-*p*-toluenesulphonamides lack the acidic hydrogen and do not form a soluble anion with base while 3° amines would yield highly unstable cationic quarternary sulphonamides.

64. (d): 1-Aminobutane is a 1°-amine has the highest boiling point due to more association by H-bonding.

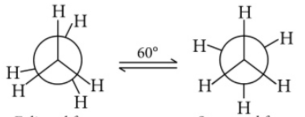
65. (b): 1°-Amine having the same no. of carbon atoms can be obtained by the reduction of amides by $LiAlH_4$.

$$\underset{\substack{\text{Acetamide}\\\text{(Ethanamide)}}}{CH_3CONH_2} + 4[H] \xrightarrow{LiAlH_4} \underset{\substack{\text{Ethyl amine}\\\text{(Ethanamine)}}}{CH_3CH_2NH_2} + H_2O$$

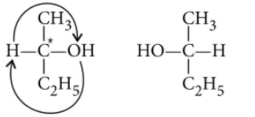
66. (e) : (A)

$$\underset{\substack{\text{Acetaldehyde}\\\text{(Keto form, 100\%)}}}{CH_3—\overset{\overset{\displaystyle O}{||}}{C}—H} \underset{}{\overset{\text{Tautomerisation}}{\rightleftharpoons}} \underset{\substack{\text{Vinyl alcohol}\\\text{(Enolic form)}}}{CH_2{=}\overset{\overset{\displaystyle OH}{|}}{C}—H}$$

(B) Conformational isomers



Eclipsed form — Staggered form

(C) 

(+)-2-Butanol — (–)-2-Butanol

(Enantiomeric forms)

(D) $\underset{\text{Methyl } n\text{-propyl amine}}{C_3H_7—NH—CH_3}$; $\underset{\text{Diethylamine}}{C_2H_5—NH—C_2H_5}$

(Both are metamers)

67. (a)

68. (a)

69. (c) :

Amino acid	Letter code
Glycine	G
Valine	V
Tryptophan	W
Histidine	H
Alanine	A

70. (c) : Due to the deficiency of vitamin B_2 or G (Riboflavin), cheilosis (*i.e.* cracking of lips and corners of the mouth) and digestive disorders occur.

71. (e) : Except tetracycline, the other given drugs are bactericidal.

72. (d): $\underset{\substack{\text{Tetrachloromethane}\\\text{(Carbon tetrachloride)}}}{3CCl_4} + 2SbF_3 \xrightarrow[\text{Swartz reaction}]{SbCl_5,\ \Delta} \underset{\text{Freon-12}}{3CCl_2F_2} + 2SbCl_3$

2015 CBSE-BOARD

CHAPTERWISE PRACTICE PAPER

Series-2 **Electrochemistry | Chemical Kinetics**

Time : 3 hrs. Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
(iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
(iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
(v) Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
(vi) Use Log Tables, if necessary. Use of calculator is not allowed.

1. The rate constant of a reaction is 3×10^{-4} L mol^{-1} min^{-1}. What is the order of the reaction?

2. How much electricity is required in coulombs for the oxidation of 1 mole of H_2O to O_2?

3. What is meant by an elementary reaction?

4. What will happen to the value of emf of the cell Zn | Zn^{2+} (0.1 M) || Cu^{2+} (0.1 M) | Cu, if the concentration of the electrolyte in the anode compartment is increased?

5. Why does the rate of a reaction not remain constant throughout the reaction process?

6. Why is hydrogen electrode used as reference electrode?

7. Define "order of the reaction".

8. What is primary cell? Give an example.

9. A first order reaction takes 160 minutes time for 20% completion. Calculate the time required for half completion of the reaction.

10. Given the standard electrode potentials,
$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V,
$Hg^{2+}/Hg = 0.79$ V, $Mg^{2+}/Mg = -2.37$ V,
$Cr^{3+}/Cr = -0.74$ V
Arrange these metals in their increasing order of reducing power.

11. Why is it that the instantaneous rate of a reaction does not change when a part of the reacting solution is taken out?

12. The measured resistance of a conductance cell containing 7.5×10^{-3} M solution of KCl at 25 °C was 1005 ohm. Calculate
    (i) specific conductance
    (ii) molar conductance of the solution (cell constant = 1.25 cm^{-1}).

13. Rate constant, k of a reaction varies with temperature according to the equation :
$$\log k = \text{Constant} - \frac{E_a}{2.303\,R}\cdot\frac{1}{T}$$
where, E_a is the energy of activation for the reaction. When a graph is plotted for $\log k$ vs $\frac{1}{T}$ a straight line with a slope – 6670 K is obtained. Calculate energy of activation for this reaction. State the units. ($R = 8.314$ J K^{-1} mol^{-1})

14. (i) State the factors that influence the value of cell potential of the following cell :
$Mg_{(s)} \mid Mg^{2+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$
(ii) Write Nernst equation to calculate the cell potential of the above cell.

15. What is activation energy? How is the activation energy affected by
(i) the use of catalyst and
(ii) a rise in temperature?

16. Why does the conductivity of a solution decrease with dilution?

17. The activation energy of a reaction is 75.2 kJ mol^{-1} in the absence of a catalyst and 50.14 kJ mol^{-1} with a catalyst. How many times will the rate of reaction increase in the presence of the catalyst if the reaction proceeds at 25 °C?
[$R = 8.314$ J K^{-1} mol^{-1}]

OR

The following initial rate data were obtained at 300 K for the reaction : $2A + B \rightarrow C + D$.

	$[A]$/mol L^{-1}	$[B]$/mol L^{-1}	Rate/mol L^{-1} s^{-1}
I	0.2	0.1	6.0×10^{-2}
II	0.4	0.1	2.4×10^{-1}
III	0.2	0.2	1.2×10^{-1}

(i) Deduce the rate law.
(ii) If half life of reaction is inversely proportional to initial concentration of the reactant, what is the order of the reaction?

18. Can you store copper sulphate solution in a zinc pot?

19. The decomposition of NH_3 on platinum surface
$$2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$$
is a zero order reaction with $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}. What are the rates of production of N_2 and H_2?

20. How much charge is required for the following reductions :
(i) 1 mol of Al^{3+} to Al ?
(ii) 1 mol of Cu^{2+} to Cu ?
(iii) 1 mol of MnO_4^- to Mn^{2+} ?

21. The rate constant for the decomposition of a hydrocarbon is 2.418×10^{-5} s^{-1} at 546 K. If the energy of activation is 179.9 kJ / mol, what will be the value of pre-exponential factor?

22. Calculate the E.M.F of the following cell at 298 K.
Fe | Fe^{2+} (0.1M) || Ag^{+}(0.1M) | Ag
Given : $E^{\circ}_{Fe^{2+}/Fe} = -0.44$ V, $E^{\circ}_{Ag^{+}/Ag} = 0.8$ V
($R = 8.31$ J K^{-1} mol^{-1} and F = 96500 C mol^{-1})

23. The data given below is for the reaction,
$2N_2O_{5(g)} \rightleftharpoons 4NO_{2(g)} + O_{2(g)}$ at 298 K

S. No.	$[N_2O_5]$/ (mol L^{-1})	Rate of disappearance of N_2O_5/(mol L^{-1} min^{-1})
1.	1.13×10^{-2}	34×10^{-5}
2.	0.84×10^{-2}	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

For this reaction determine
(i) order of the reaction
(ii) rate constant
(iii) rate law.

24. Mr. Sohan went with his son Bikky to the market. Sohan requested to a shopkeeper to give him batteries. The shopkeeper showed them two types of batteries. One battery made with lead plates was cheaper whereas the other battery made of cadmium black was costlier. Mr. Sohan wanted to purchase the lead plated battery as it was cheaper. But Bikky insisted to purchase cadmium plated costlier battery.
Now answer the following questions :
(i) What is a battery?
(ii) Why Bikky insisted to purchase costlier battery?
(iii) What are the values associated with the above decision?

25. A reaction is first order w.r.t. A and second order w.r.t. B.
(i) Write the differential rate equation.
(ii) How is the rate affected on increasing the concentration of B three times?
(iii) How is the rate affected when the concentration of both A and B are doubled?

26. Calculate the half - life of the first order reactions from their rate constants given below :

(i) 200 s^{-1} **(ii)** 2 min^{-1}

(iii) 4 years^{-1}

27. Resistance of a conductivity cell filled with 0.1 M KCl solution is 100 ohm. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 ohm, calculate the conductivity and molar conductivity of 0.02 M KCl solution. Conductivity of 0.1 M KCl solution is 1.29 S m^{-1}.

OR

Silver is electrodeposited on a metallic vessel of total surface area 900 cm^2 by passing a current of 0.2 amp for two hours. Calculate the thickness of silver deposited. [Given : Density of silver = 10.5 g cm^{-3}, Atomic mass of silver = 108 amu, F = 96500 C mol^{-1}]

28. **(i)** For a chemical reaction, what is the effect of a catalyst on the following :

(a) Activation energy of the reaction

(b) Rate constant of the reaction.

(ii) The rate of a reaction increases four times when the temperature changes from 300 K to 320 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

[$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]

OR

(i) Show that for a first order reaction the time required for half the change (half life period) is independent of initial concentration.

(ii) Show that in a first order reaction, time required for completion of 99.9% is 10 times of half time ($t_{1/2}$) of the reaction.

29. **(i)** State Kohlrausch's law for electrical conductance of an electrolyte at infinite dilution.

(ii) The equivalent conductances of sodium acetate, sodium chloride and hydrochloric acid are 83, 127 and 426 mho $\text{cm}^2 \text{ eq}^{-1}$ at 250°C respectively. Calculate the equivalent conductance of acetic acid solution.

OR

(i) The E° values in respect of electrodes of chromium (Z = 24), manganese (Z = 25) and iron (Z = 26) are :

$Cr^{3+}/Cr^{2+} = -0.4$ V ; $Mn^{3+}/Mn^{2+} = +1.5$ V ; $Fe^{3+}/Fe^{2+} = 0.8$ V. On the basis of the above information compare the feasibilities of further oxidation of their + 2 oxidation states.

(ii) Calculate standard electrode potential for the half cell $Fe^{3+} + 3e^- \rightleftharpoons Fe$ from the following data :

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$; $E^\circ = 0.77$ V

$Fe^{2+} + 2e^- \rightleftharpoons Fe$; $E^\circ = -0.44$ V

30. **(i)** At 380 °C, the half life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450 °C.

(ii) A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate $t_{1/2}$ value for it.

OR

(i) A reaction is second order with respect to a reactant. How will the rate of reaction be affected if the concentration of this reactant is

(a) doubled **(b)** reduced to half.

(ii) The decomposition of phosphine (PH_3), proceeds according to the following equation :

$$4PH_{3(g)} \rightarrow P_{4(s)} + 6H_{2(g)}$$

It is found that the reaction follows the rate equation : Rate = $k[PH_3]$

The half life period of PH_3 is 37.9 s at 120 °C.

(a) How much time is required for $\frac{3}{4}$th of PH_3 to decompose?

(b) What fraction of the original sample of PH_3 remains behind after 1 minute?

SOLUTIONS

1. The unit of second order rate constant is $L\ mol^{-1}\ min^{-1}$, therefore $k = 3 \times 10^{-4}\ L\ mol^{-1}\ min^{-1}$ represents a second order reaction.

2. The electrode reaction for oxidation of 1 mole of H_2O is

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$$

$\therefore$ Quantity of electricity required = 2 F
= 2 × 96500 = 193000 C

3. A reaction which takes place in one step is called elementary reaction.

4. EMF of the cell decreases as

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303\ RT}{nF}\log\frac{[M^{n+}]\text{ anode}}{[M^{n+}]\text{ cathode}}$$

5. With the progress of reaction, concentration of reactant decreases, hence rate of reaction also decreases.

6. Because the standard electrode potential of hydrogen electrode is arbitrarily taken zero in the standard conditions.

7. The sum of powers of the concentrations of the reactants in the rate law expression is called the order of that chemical reaction.

8. Primary cells are those in which the redox reaction occurs only once and the cell becomes dead after sometime, and cannot be recharged again *e.g.*, Dry cell, Mercury cell.

9. Given : $[R]_0 = 1$, $[R] = 0.8$, $t = 160$ min
$t_{1/2} = ?$

For first order reaction, $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$

or, $k = \frac{2.303}{160}\log\frac{1}{0.8}$

or, $k = \frac{2.303}{160\text{ min}} \times \log 1.25$

or, $k = \frac{2.303 \times 0.0969}{160\text{ min}} = 1.39 \times 10^{-3}\ min^{-1}$

Again, $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.39 \times 10^{-3}} = 498.56$ min

10. Lower the electrode potential of a metal greater is reducing power. The metals are arranged in the increasing order of their reducing power :

Ag < Hg < Cr < Mg < K

11. Because in instantaneous rate, the time interval is made infinitesimally small hence the change in concentration (dx) in that time interval (dt) remains the same even if a part of the reaction solution is taken out. Due to the same value of dx/dt, the instantaneous rate does not change after taking out a part of the solution.

12. (i) Specific conductance = Cell constant/R

$$\kappa = \frac{1.25}{1005} = 0.001243\ ohm^{-1}\ cm^{-1}$$

(ii) Molar conductance $= \frac{\kappa \times 1000}{M}$

$$= \frac{0.001243 \times 1000}{7.5 \times 10^{-3}}$$

$= 165.73\ ohm^{-1}\ cm^2\ mol^{-1}$

13. Slope of the line $= \frac{-E_a}{2.303\ R} = -6670$ K (Given)

$\therefore$ $E_a = 2.303\ R \times 6670$ K
$= 2.303 \times 8.314\ J\ K^{-1}\ mol^{-1} \times 6670$ K
$= 127711.43\ J\ mol^{-1}$
$= 127.71\ kJ\ mol^{-1}$

14. (i) Cell potential depends on the concentration of the electrolytes containing Mg^{2+} and Ag^+ ions and the temperature at which the cell is operated.

(ii) $E_{cell} = E^{\circ}_{cell} - \frac{2.303\ RT}{nF}\log\frac{[Mg^{2+}_{(aq)}]}{[Ag^+_{(aq)}]^2}$

[Here, $n = 2$]

15. The minimum amount of energy which must be supplied to the reactants to enable them to cross over the energy barrier between reactants and products is called activation energy.
Activation energy =
Threshold energy – Average energy of reactants
(i) Activation energy of the reactants decreases by the use of catalyst.
(ii) Activation energy of the reactants decreases with rise in temperature.

16. Conductivity of a solution is the conductance of unit volume of a solution. On dilution, number of ions per unit volume decreases hence conductivity decreases on dilution of solution.

17. $$k = Ae^{-E_a/RT}$$

In the absence of catalyst, $k_1 = Ae^{-75.2/RT}$

In the presence of catalyst, $k_2 = Ae^{-50.14/RT}$

$$\therefore \quad \frac{k_1}{k_2} = \frac{e^{-75.2/RT}}{e^{-50.14/RT}} = e^{-25.06/RT}$$

$$2.303 \log \frac{k_2}{k_1} = \frac{25.06}{RT}$$

$$\log \frac{k_2}{k_1} = \frac{25.06}{2.303 \times 8.314 \times 10^{-3} \times 298}$$

$$\log \frac{k_2}{k_1} = 4.3920$$

$$\frac{k_2}{k_1} = 24660$$

Thus, rate of reaction increases by 24660 times.

OR

(i) Let the rate law for the given reaction be

Rate $= k[A]^x[B]^y$

Then, $\dfrac{r_{II}}{r_I} = \dfrac{2.4 \times 10^{-1}}{6.0 \times 10^{-2}} = \dfrac{k(0.4)^x \times (0.1)^y}{k(0.2)^x \times (0.1)^y}$

$4 = 2^x \quad \Rightarrow \quad x = 2$

Again, $\dfrac{r_{III}}{r_I} = \dfrac{1.2 \times 10^{-1}}{6.0 \times 10^{-2}} = \dfrac{k(0.2)^x \times (0.2)^y}{k(0.2)^x \times (0.1)^y}$

or, $\quad 2 = 2^y \quad \Rightarrow \quad y = 1$

Hence, the rate law $= k[A]^2[B]^1$

(ii) If half life period is inversely proportional to the initial concentration, then the order of the reaction is 2.

18. No we cannot store $CuSO_4$ solution in a zinc pot because zinc is more reactive ($E^\circ_{Zn^{2+}/Zn} =$ – 0.76 V) than Cu($E^\circ_{Cu^{2+}/Cu} = 0.34$ V). Hence Zn will displace Cu from $CuSO_4$ solution.

$CuSO_{4(aq)} + Zn_{(s)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$

19. $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

$k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

The order of reaction is zero *i.e.*,

Rate $= k$ [Reactant]^0

Rate $= 2.5 \times 10^{-4} \times 1$

$= 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

$$\therefore \quad \text{Rate of reaction} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$$

The rate of formation of N_2

$= 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

$$\text{Again, } 2.5 \times 10^{-4} = \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\therefore \quad \frac{d[H_2]}{dt} = 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Therefore, rate of formation of H_2

$= 7.5 \times 10^{-4}$ mol L^{-1} s^{-1}

20. (i) $\underset{1 \text{ mole}}{Al^{3+}} + \underset{3 \text{ moles}}{3e^-} \rightarrow Al$

$\therefore$ 3 moles of electrons are needed for reduction of 1 mole of Al^{3+} to Al.

3 moles of electrons = 3 Faradays

$= 3 \times 96500$ Coulombs

$= 2.895 \times 10^5$ Coulombs

(ii) $\underset{1 \text{ mole}}{Cu^{2+}} + \underset{2 \text{ moles}}{2e^-} \rightarrow Cu$

$\therefore$ 2 moles of electrons are needed for reduction of 1 mole of Cu^{2+} to Cu.

2 moles of electrons = 2 Faradays

$= 2 \times 96500$ Coulombs

$= 1.93 \times 10^5$ Coulombs

(iii) $\underset{1 \text{ mole}}{MnO^-_{4(aq)}} + 8H^+ + \underset{5 \text{ moles}}{5e^-} \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$

$\therefore$ 5 moles of electrons are needed for reduction of 1 mole of MnO_4^- to Mn^{2+}.

5 moles of electrons = 5 Faradays

$= 5 \times 96500$ Coulombs

$= 4.825 \times 10^5$ Coulombs

21. According to Arrhenius equation :

$$k = A.e^{-E_a/RT}$$

$$\text{or,} \quad \log k = \log A - \frac{E_a}{2.303\ RT}$$

Given : $k = 2.418 \times 10^{-5}$ s^{-1}, $T = 546$ K,

$E_a = 179.9$ kJ mol^{-1} = 179900 J mol^{-1}

$R = 8.314$ J K^{-1} mol^{-1}

Putting the values in the equation,
$\log (2.418 \times 10^{-5}\ s^{-1})$

$$= \log A - \frac{179900\ J\ mol^{-1}}{2.303 \times 8.314\ J K^{-1}\ mol^{-1} \times 546\ K}$$

$- 4.6165\ s^{-1} = \log A - 17.2082$
$\log A = 17.2082 - 4.6165 = 12.5917$
$A = 3.91 \times 10^{12}\ s^{-1}$

22. $Fe \mid Fe^{2+}\ (0.1M) \parallel Ag^+\ (0.1M) \mid Ag$

$E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Fe^{2+}/Fe}$
$= 0.8\ V - (-0.44\ V) = 0.8\ V + 0.44\ V = 1.24\ V$

$$E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{nF} \log \frac{[Fe^{2+}]}{[Ag^+]^2}$$

Here, value of $n = 2$

$$E_{cell} = E^\circ_{cell} - \left(\frac{2.303 \times 8.31 \times 298}{2 \times 96500}\right) \log \frac{(0.1\ M)}{(0.1\ M)^2}$$

$$= E^\circ_{cell} - \frac{0.0591}{2} \log \frac{(0.1)}{(0.01)}$$

$= 1.24\ V - 0.02955 \times \log 10$
$= 1.24\ V - 0.02955\ V \qquad [\because \log 10 = 1]$
$= 1.21\ V$

23. **(i)** Let rate law for the reaction be,
Rate $= k[N_2O_5]^a$

Then $\frac{r_1}{r_2} = \frac{34 \times 10^{-5}}{25 \times 10^{-5}} = \frac{k\ (1.13 \times 10^{-2})^a}{k (0.84 \times 10^{-2})^a}$

or, $\frac{34}{25} = \left(\frac{113}{84}\right)^a$ or $a \approx 1$

Thus, order of reaction = 1

(ii) $r = k[N_2O_5]$ or, $34 \times 10^{-5} = k \times 1.13 \times 10^{-2}$

or, $k = \frac{34 \times 10^{-5}}{1.13 \times 10^{-2}} = 3.0 \times 10^{-2}\ min^{-1}$

(iii) Rate law $= k[N_2O_5]$

24. **(i)** Battery is a type of electrochemical cell which is used to produce electricity.

(ii) Lead is a serious pollutant. Lead salts are insoluble in water. If it is ingested into a body it causes cancer. Cadmium is less pollutant. Cd salts are soluble in water. It causes less toxic effect. This is why Bikky insisted his father to purchase expensive battery.

(iii) We must always keep safety of environment in mind.

25. The reaction is first order w.r.t. A and second order w.r.t. B.

(i) Differential rate equation is
Rate $= k[A][B]^2$

(ii) The new concentration of $B = [3B]$
$\therefore$ New rate $= k[A][3B]^2 = 9k[A][B]^2$
$\therefore$ New rate = 9 times of the original rate

(iii) New concentration of $A = [2A]$
New concentration of $B = [2B]$
$\therefore$ New rate $= k[2A][2B]^2 = 8k[A][B]^2$
$\therefore$ New rate = 8 times of the original rate

26. For a first order reaction, $t_{1/2} = \frac{0.693}{k}$

(i) $k = 200\ s^{-1}$

$\therefore\ t_{1/2} = \frac{0.693}{200\ s^{-1}} = 3.46 \times 10^{-3}\ s$

(ii) $k = 2\ min^{-1}$

$\therefore\ t_{1/2} = \frac{0.693}{2\ min^{-1}} = 3.46 \times 10^{-1}\ min$

(iii) $k = 4\ years^{-1}$

$\therefore\ t_{1/2} = \frac{0.693}{4\ year^{-1}} = 1.73 \times 10^{-1}$ year

27. Resistance of 0.1 M KCl solution, $R = 100\ \Omega$
Conductivity, $\kappa = 1.29\ S\ m^{-1}$
Cell constant, $G^* = \kappa \times R = 1.29 \times 100 = 129\ m^{-1}$
Resistance of 0.02 M KCl solution, $R = 520\ \Omega$

Conductivity, $\kappa = \frac{\text{Cell constant}}{R}$

$= \frac{129\ m^{-1}}{520\ \Omega} = 0.248\ S\ m^{-1}$

Concentration, $C = 0.02 \frac{\text{mole}}{\text{litre}}$
$= 1000 \times 0.02\ mol\ m^{-3}$
$= 20\ mol\ m^{-3}$

Molar conductivity, $\Lambda_m = \frac{\kappa}{C} = \frac{0.248\ S m^{-1}}{20\ mol\ m^{-3}}$
$= 0.0124\ S\ m^2\ mol^{-1}$

OR

$Ag^+ + e^- \rightarrow Ag$ (Electrode reaction)

Amount of charge passed = Current × Time

$= 0.2\ A \times 2 \times 60 \times 60 = 1440\ C$

From the electrode reaction,

96500 C of charge deposit Ag = 108 g

1440 C of charge deposit Ag

$$= \frac{108 \times 1440}{96500} = 1.61\ g$$

Mass = Volume × Density

= Area × Thickness × Density

$$\therefore \quad \text{Thickness} = \frac{\text{Mass}}{\text{Area} \times \text{Density}} = \frac{1.61}{900 \times 10.5}$$

$$= 1.7 \times 10^{-4}\ \text{cm}$$

28. (i) **(a)** A catalyst decreases the activation energy.

(b) A catalyst does not change the rate constant of a reaction.

(ii) Given : $r_2 = 4r_1$, $T_1 = 300$ K, $T_2 = 320$ K

$E_a = ?$

Using Arrhenius equation :

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_2 \times T_1}\right)$$

$$\text{or, } \log \frac{4k_1}{k_1} = \frac{E_a}{2.303 \times 8.314}\left(\frac{20}{320 \times 300}\right)$$

$$\text{or, } 0.6020 = \frac{E_a}{19.147} \times \frac{1}{4800}$$

or, $E_a = 0.6020 \times 19.147 \times 4800$

$E_a = 55.327\ \text{kJ mol}^{-1}$

OR

(i) For first order reaction, $k = \dfrac{2.303}{t} \log \dfrac{[R]_0}{[R]}$

when $t = t_{1/2}$, $[R] = \dfrac{[R]_0}{2}$

$$\text{or, } k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R_0]/2}$$

$$\text{or, } k = \frac{2.303}{t_{1/2}} \log 2$$

$$\text{or, } t_{1/2} = \frac{2.303 \log 2}{k} = \frac{2.303 \times 0.3010}{k}$$

$$= \frac{0.693}{k}$$

Thus, half life period of first order reaction is independent of initial concentration.

(ii) When reaction is 99.9% completed.

$[R]_t = [R]_0 - 0.999\,[R]_0 = 0.001\,[R]_0$

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$$

$$\Rightarrow k = \frac{2.303}{t} \log \frac{[R]_0}{0.001\,[R]_0}$$

$$\text{or, } t = \frac{2.303}{k} \log 10^3$$

$$t = \frac{2.303 \times 3}{k} = \frac{6.909}{k} \qquad \text{...(i)}$$

$$\text{For half life, } t_{1/2} = \frac{0.693}{k} \qquad \text{...(ii)}$$

Dividing (i) by (ii)

$$\frac{t}{t_{1/2}} = \frac{\frac{6.909}{k}}{\frac{0.693}{k}} \Rightarrow \frac{t}{t_{1/2}} = 10 \text{ or, } t = 10.t_{1/2}$$

29. (i) Kohlrausch's law states that at infinite dilution, when the dissociation of electrolyte is complete, each ion makes a definite contribution towards the molar conductivity of electrolyte, irrespective of the nature of other ion with which it is associated.

$$\Lambda_m^{\infty} = \mu_+\lambda_+^{\infty} + \mu_-\lambda_-^{\infty}$$

(ii) Given :

$\Lambda^\circ(CH_3COONa) = 83$ mho cm^2 eq^{-1}

$\Lambda^\circ(NaCl) = 127$ mho cm^2 eq^{-1}

$\Lambda^\circ(HCl) = 426$ mho cm^2 eq^{-1}

$\Lambda^\circ(CH_3COOH) = ?$

Using Kohlrausch law of independent migration of ions,

$\Lambda^\circ(CH_3COOH)$

$= \Lambda^\circ(CH_3COONa) + \Lambda^\circ(HCl) - \Lambda^\circ(NaCl)$

or, $\Lambda^\circ(CH_3COOH) = 83 + 426 - 127$

$= 382$ mho cm^2 eq^{-1}

OR

(i) From electrode potential data it is obvious that +2 oxidation state of Mn is more stable than +2 oxidation state of Fe which in turn is more stable than +2 oxidation state of Cr, so the order of feasibility of further oxidation of +2 oxidation state is $Cr^{2+} > Fe^{2+} > Mn^{2+}$.

(ii) Given equations are

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}; E_1^\circ = +0.77$ V

$Fe^{2+} + 2e^- \rightleftharpoons Fe; E_2^\circ = -0.44$ V

The desired equation is

$Fe^{3+} + 3e^- \rightleftharpoons Fe; E_3^\circ = ?$

The desired equation is obtained by adding above two equations.

$$\text{Therefore, } E_3^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3}$$

$$\text{or, } E_3^\circ = \frac{1 \times 0.77\text{ V} + 2 \times (-0.44\text{ V})}{3}$$

$$= \frac{-0.11}{3} = -0.04\text{ V}$$

30. (i) $$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{360\,\text{min}} = 1.92 \times 10^{-3}\,\text{min}^{-1}$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\frac{k_2}{k_1} = \frac{200000}{19.147} \times \frac{723 - 653}{723 \times 653} = 1.5487$$

$$\frac{k_2}{k_1} = \text{Antilog}\,(1.5487) = 35.38$$

$$k_2 = k_1 \times 35.38 = 1.92 \times 10^{-3} \times 35.38$$

$$= 6.792 \times 10^{-2}\,\text{min}^{-1}$$

$$t = \frac{2.303}{k_2}\log\frac{[R]_0}{\frac{25}{100}[R]_0}$$

$$= \frac{2.303}{6.792 \times 10^{-2}\,\text{min}^{-1}} \times 0.6021$$

$$= 20.415\text{ min}$$

(ii) $$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} = \frac{2.303}{40}\log\frac{100}{70}$$

$$= \frac{2.303}{40}\log\frac{10}{7} = \frac{2.303}{40}(\log 10 - \log 7)$$

$$= \frac{2.303}{40}(1 - 0.845) = \frac{2.303}{40}(0.155)$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693 \times 40}{2.303 \times 0.155}$$

$$= 77.7\text{ minutes}$$

OR

(i) Rate $= k[R]^2$

(a) If $[R] = [2R]$, rate $= k[2R]^2 = 4k[R]^2$

i.e. rate of reaction increases 4 times when concentration is doubled.

(b) If $[R] = \left[\frac{R}{2}\right]$, rate $= k\left[\frac{R}{2}\right]^2 = \frac{1}{4}k[R]^2$

i.e., rate becomes $\frac{1}{4}$th when concentration is reduced to $\frac{1}{2}$.

(ii) Given : Rate $= k[PH_3]$, $t_{1/2} = 37.9$ s

(a) $t = ?$ when $[R] = \frac{1}{4}[R]_0$

$$\text{Using formula } \frac{[R]}{[R]_0} = \left(\frac{1}{2}\right)^n$$

$$\frac{\frac{1}{4}[R]_0}{[R]_0} = \left(\frac{1}{2}\right)^n \text{ or, } \frac{1}{4} = \left(\frac{1}{2}\right)^n \text{ or, } n = 2$$

Again $t = n \times t_{1/2} = 2 \times 37.9\text{ s} = 75.8$ s

(b) $t = 60$ s (1 min.) $= \frac{[R]}{[R]_0} = ?$

$$\text{Using formula } k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

$$\frac{0.693}{37.9\text{ s}} = \frac{2.303}{60\text{ s}}\log\frac{[R]_0}{[R]}$$

$$\text{or, } \log\frac{[R]_0}{[R]} = \frac{0.693}{37.9\text{ s}} \times \frac{60\text{ s}}{2.303} = 0.476$$

$$\text{or, } \log\frac{[R]}{[R]_0} = -0.476$$

$$\text{or, } \frac{[R]}{[R]_0} = \text{antilog}(-0.476)$$

$$\Rightarrow \frac{[R]}{[R]_0} = 0.3342$$

EXAMINER'S MIND NCERT CLASS XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

ELECTROCHEMISTRY | CHEMICAL KINETICS

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. $E°$ values of three metals are listed below :

$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$; $E° = -0.76$ V

$Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$; $E° = -0.44$ V

$Sn^{2+}_{(aq)} + 2e^- \longrightarrow Sn_{(s)}$; $E° = -0.14$ V

Which of the following statements are correct on the basis of the above information?

(i) Zinc will be corroded in preference to iron if zinc coating is broken on the surface.

(ii) If iron is coated with tin and the coating is broken on the surface then iron will be corroded.

(iii) Zinc is more reactive than iron but tin is less reactive than iron.

(a) (i) and (ii) (b) (ii) and (iii)
(c) (i), (ii) and (iii) (d) (i) and (iii)

2. In a homogeneous reaction $A \rightarrow B + C + D$, the initial pressure was P_0 and after time t it was P. Expression for rate constant k in terms of P_0, P and t will be

(a) $k = \dfrac{2.303}{t}\log\dfrac{2P_0}{3P_0 - P}$

(b) $k = \dfrac{2.303}{t}\log\dfrac{2P_0}{P_0 - P}$

(c) $k = \dfrac{2.303}{t}\log\dfrac{3P_0 - P}{2P_0}$

(d) $k = \dfrac{2.303}{t}\log\dfrac{2P_0}{3P_0 - 2P}$

3. On passing C ampere of current for time t sec through 1 litre of 2 M $CuSO_4$ solution (atomic weight of Cu = 63.5), the amount m of Cu (in g) deposited on cathode will be

(a) $m = \dfrac{Ct}{(63.5\times 96500)}$

(b) $m = \dfrac{Ct}{(31.25\times 96500)}$

(c) $m = \dfrac{C\times 96500}{(31.25\times t)}$

(d) $m = \dfrac{31.75\times C\times t}{96500}$

4. The role of a catalyst is to change

(a) Gibbs energy of reaction
(b) enthalpy of reaction
(c) activation energy of reaction
(d) equilibrium constant.

5. The time required to coat a metal surface of 80 cm^2 with 5×10^{-3} cm thick layer of silver (density 1.05 g cm^{-3}) with a passage of 3 A current through a silver nitrate solution is

(a) 115 sec (b) 125 sec
(c) 135 sec (d) 145 sec

6. For the reaction $X + Y \longrightarrow P$, the rate law is expressed as rate = $k[X][Y]^2$. Which of the following statements will be false for the reaction?

(a) If $[Y]$ is held constant and $[X]$ is doubled, reaction rate will be doubled.

(b) If $[X]$ is held constant and $[Y]$ is reduced to one-fourth, the rate of reaction will be halved.

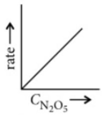
(c) If $[X]$ and $[Y]$ both are doubled, the rate of reaction will be increased by 8 times.
(d) This reaction is of third order.

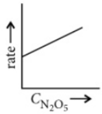
7. Consider the following four electrodes :
$P = Cu^{2+}\ (0.0001\ M)/Cu_{(s)}$
$Q = Cu^{2+}\ (0.1\ M)/Cu_{(s)}$
$R = Cu^{2+}\ (0.01\ M)/Cu_{(s)}$
$S = Cu^{2+}\ (0.001\ M)/Cu_{(s)}$
If the standard reduction potential of Cu^{2+}/Cu is +0.34 V, the reduction potentials in volts of the above electrodes follow the order
(a) $P > S > R > Q$ (b) $S > R > Q > P$
(c) $R > S > Q > P$ (d) $Q > R > S > P$

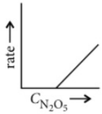
8. The decomposition of a substance R takes place according to first order kinetics. Its initial concentration is reduced to $1/8^{\text{th}}$ in 24 s. The rate constant of the reaction is
(a) $\frac{1}{24}\,s^{-1}$ (b) $\frac{0.69}{16}\,s^{-1}$
(c) $\frac{\ln 2}{8}\,s^{-1}$ (d) $\frac{1}{8}\,s^{-1}$

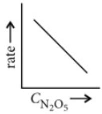
9. For a certain redox reaction, $E°$ is positive. This means that
(a) $\Delta G°$ is positive, K is greater than 1
(b) $\Delta G°$ is positive, K is less than 1
(c) $\Delta G°$ is negative, K is greater than 1
(d) $\Delta G°$ is negative, K is less than 1.

10. Which one of the following plots is true for the first order decomposition of N_2O_5?

(a) 

(b) 

(c) 

(d) 

11. Which of the statements about solutions of electrolytes is not correct?
(a) Conductivity of solution depends upon size of ions.
(b) Conductivity depends upon viscosity of solution.
(c) Conductivity does not depend upon solvation of ions present in solution.
(d) Conductivity of solution increases with temperature.

12. For a first order reaction, $A \rightarrow$ products, the rate of reaction at $[A] = 0.2$ M is 1.0×10^{-2} mol litre^{-1} min^{-1}. The half-life period for the reaction is
(a) 832 sec (b) 440 sec
(c) 416 sec (d) 14 sec

13. The equivalent conductances at infinite dilution for AC, BD and CD are 91, 426.2 and 126.5 ohm^{-1} cm^2 g-eqiv^{-1} respectively. Then the equivalent conductance of AB will be (in ohm^{-1} cm^2 g-eqiv^{-1})
(a) 517.2 (b) 390.7
(c) 335.2 (d) 300

14. Of the following, which is a second order reaction?
(a) $k = 5.47 \times 10^{-4}\ s^{-1}$
(b) $k = 3.9 \times 10^{-3}\ mol\ L\ s^{-1}$
(c) $k = 3.94 \times 10^{-4}\ L\ mol^{-1}\ s^{-1}$
(d) $k = 3.98 \times 10^{-5}\ L\ mol^{-2}\ s^{-2}$

15. The standard reduction potentials for the following half-cell reactions are
$Zn^{2+} + 2e^- \longrightarrow Zn;\ E° = -0.76$ V;
$Fe^{2+} + 2e^- \longrightarrow Fe;\ E° = -0.44$ V
The e.m.f. for the cell reaction :
$Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$ will be
(a) +1.20 V (b) +0.32 V
(c) −0.32 V (d) −1.20 V

16. $t_{1/2}$ for a first order reaction is 14.26 mins. The percentage of reactant decomposed after 50 s is
(a) 8% (b) 4%
(c) 6% (d) 10.2%

17. Standard reduction potentials of the half reactions are given below :
$F_{2(g)} + 2e^- \longrightarrow 2F^-_{(aq)}\ ;\ E° = +2.85$ V
$Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}\ ;\ E° = +1.36$ V
$Br_{2(l)} + 2e^- \longrightarrow 2Br^-_{(aq)}\ ;\ E° = +1.06$ V
$I_{2(s)} + 2e^- \longrightarrow 2I^-_{(aq)}\ ;\ E° = +0.53$ V
The strongest oxidising and reducing agents are respectively
(a) F_2 and I^- (b) Br_2 and Cl^-
(c) Cl_2 and Br^- (d) Cl_2 and I_2

18. The experimental data for the reaction :

$2A + B_2 \longrightarrow 2AB$ is

Exp.	$[A]$ (mol L^{-1})	$[B_2]$ (mol L^{-1})	Rate (mol L^{-1} s^{-1})
1	0.50	0.50	1.6×10^{-4}
2	0.50	1.00	3.2×10^{-4}
3	1.00	1.00	3.2×10^{-4}

The rate equation for the above data is

(a) rate $= k[A]^2[B_2]^2$ (b) rate $= k[A]^2[B_2]$

(c) rate $= k[B_2]$ (d) rate $= k[B_2]^2$

19. Molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. The degree of dissociation and dissociation constant will be (Given : $\lambda^\circ_{H^+} = 349.6$ S cm^2 mol^{-1} and $\lambda^\circ_{HCOO^-} = 54.6$ S cm^2 mol^{-1})

(a) 11.4%, 3.67×10^{-4}

(b) 22.8%, 1.83×10^{-4}

(c) 52.2%, 4.25×10^{-4}

(d) 1.14%, 3.67×10^{-6}

20. Which of the following statements is not correct about order of a reaction?

(a) The order of a reaction can be a fractional number.

(b) The order of a reaction is experimentally determined quantity.

(c) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.

(d) The order of a reaction is the sum of the powers of molar concentrations of the reactants in the rate law expression.

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. Which of the following statements is true for an electrochemical cell?

(a) H_2 is anode and Cu is cathode.

(b) H_2 is cathode and Cu is anode.

(c) Reduction occurs at H_2 electrode.

(d) Oxidation occurs at Cu electrode.

22. The rate constant of a reaction is given by $k = 2.1 \times 10^{10} \exp(-2700/RT)$. It means that

(a) $\log k$ vs $1/T$ will be a straight line with slope $= -\dfrac{2700}{2.303R}$

(b) $\log k$ vs $1/T$ will be a straight line with intercept on $\log k$ axis $= \log 2.1 \times 10^{10}$

(c) the number of effective collisions are 2.1×10^{10} cm^{-3} sec^{-1}

(d) half-life of a reaction increases with increase of temperature.

23. If same quantity of electricity is passed through three electrolytic cells containing $FeSO_4$, $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$, then

(a) the amount of iron deposited in $FeSO_4$ and $Fe_2(SO_4)_3$ are equal

(b) the amount of iron deposited in $FeSO_4$ is 1.5 times of the amount of iron deposited in $Fe(NO_3)_3$

(c) the amount of iron deposited in $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$ are equal

(d) the same amount of gas is evolved in all three cases at the anode.

24. Which of the following is/are incorrect regarding activation energy?

(a) Larger the activation energy, smaller is the value of rate constant.

(b) The higher the E_a, higher is the value of temperature coefficient, $\dfrac{k_{T+10}}{k_T}$.

(c) At lower temperatures, increase in temperature causes more change in the value of k than at higher temperature.

(d) A plot made between k and $1/T$ gives a straight line of slope $-(E_a/R)$.

25. For the reduction of NO_3^- ion in aqueous solution, E° is +0.96 V and values of E° for some metal ions are given below :

$V^{2+}_{(aq)} + 2e^- \longrightarrow V$, $E^\circ = -1.19$ V

$Fe^{3+}_{(aq)} + 3e^- \longrightarrow Fe$, $E^\circ = -0.04$ V

$Au^{3+}_{(aq)} + 3e^- \longrightarrow Au$, $E^\circ = +1.40$ V

$Hg^{2+}_{(aq)} + 2e^- \longrightarrow Hg$, $E^\circ = +0.86$ V

The pair(s) of metals that is(are) oxidised by NO_3^- in aqueous solution is/are

(a) V and Hg (b) Hg and Fe

(c) Fe and Au (d) Fe and V

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Most of the chemical reactions are accelerated by increase in temperature. The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation :

$$k = A\, e^{-E_a/RT}$$

where A is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and E_a is activation energy measured in joules/mole (J mol^{-1}).

26. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = A.e^{\frac{-E_a}{RT}}$. Activation energy ($E_a$) of the reaction can be calculated by plotting

(a) k *vs* T (b) k *vs* $\dfrac{1}{\log T}$

(c) $\log k$ *vs* $\dfrac{1}{T}$ (d) $\log k$ *vs* $\dfrac{1}{\log T}$

27. If for a first order reaction, the values of A and E_a are $4 \times 10^{13}\ \text{s}^{-1}$ and 98.6 kJ/mol respectively, then at what temperature will its half-life period be 10 minutes?

(a) 330 K (b) 300 K

(c) 330.95 K (d) 310.9 K

28. A chemical reaction takes place in three steps having rate constants k_1, k_2, k_3, respectively. If E_{a_1}, E_{a_2} and E_{a_3} are 50, 40 and 30 respectively in kJ and the overall rate constant $k = \dfrac{k_1 k_3}{k_2}$. The overall energy of activation is

(a) 30 kJ (b) 15 kJ

(c) 40 kJ (d) 60 kJ

Paragraph for Questions 29 to 31

The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross-section and at a distance of unit length.

Molar conductivity of a solution at a given concentration is the conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with area of cross-section A and distance of unit length.

29. Which of the following statements is correct regarding variations of molar conductivity with concentration?

(a) Molar conductivity decreases with decrease in concentration.

(b) Variation in molar conductivity of weak and strong electrolytes is same.

(c) Molar conductivity increases with decrease in concentration.

(d) When concentration of the solution approaches zero, the molar conductivity is known as conductance.

30. Two solutions of X and Y electrolytes are taken in two beakers and diluted by adding 500 mL of water. Λ_m of X increases by 1.5 times while that of Y increases by 20 times, what could be the electrolytes X and Y?

(a) $X \longrightarrow \text{NaCl}$, $Y \longrightarrow \text{KCl}$

(b) $X \longrightarrow \text{NaCl}$, $Y \longrightarrow CH_3COOH$

(c) $X \longrightarrow \text{KOH}$, $Y \longrightarrow \text{NaOH}$

(d) $X \longrightarrow CH_3COOH$, $Y \longrightarrow \text{NaCl}$

31. When water is added to an aqueous solution of an electrolyte, what is the change in specific conductivity of the electrolyte?

(a) Decreases

(b) Increases

(c) Remains same

(d) Does not depend on number of ions

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Standard electrode potentials of few half-cell reactions are given below :

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O; E^\circ = 1.51\ \text{V}$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O; E^\circ = 1.33\ V$
$Fe^{3+} + e^- \longrightarrow Fe^{2+}; E^\circ = 0.77\ V$
$Cl_2 + 2e^- \longrightarrow 2Cl^-; E^\circ = 1.36\ V$

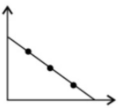
Based on the above information match the List I with List II and select the correct answer using the code given below the lists :

	List I		List II
P.	1 mol of MnO_4^- to Mn^{2+}	1.	579000 C
Q.	1 mol of $Cr_2O_7^{2-}$ to $2Cr^{3+}$	2.	193000 C
R.	1 mol of Fe^{3+} to Fe^{2+}	3.	482500 C
S.	1 mol of Cl_2 to $2Cl^-$	4.	96500 C

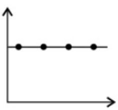
	P	Q	R	S
(a)	4	3	2	1
(b)	1	2	3	4
(c)	3	1	4	2
(d)	2	3	1	4

33. Match the List I with List II and select the correct answer using the code given below the lists :

List I **List II**

P. 

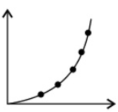
1. Initial conc. *vs* $t_{1/2}$ for zero order reaction

Q. 

2. Rate *vs* conc. for zero order reaction

R. 

3. Rate of reaction *vs* conc. of reactant for second order reaction

S. 

4. Graph plotted between ln k and $1/T$ for first order reaction

	P	Q	R	S
(a)	4	1	2	3
(b)	4	2	1	3
(c)	2	1	3	4
(d)	4	3	1	2

34. Match the List I with List II and select the correct answer using the code given below the lists :

	List I		List II
P.	$\Lambda_m^\circ(NaNO_3)$	1.	Can be obtained by Kohlrausch law
Q.	$\Lambda_m^\circ(C_2H_5COOH)$	2.	Can be obtained by extrapolating Λ_m *vs* (molarity)$^{1/2}$ graph to zero molarity
R.	Ionic mobility	3.	Contribution by the ion to Λ_m°
S.	Ionic conductance	4.	Velocity of the ion under electric field of 1 V cm^{-1}

	P	Q	R	S
(a)	4	1	2	3
(b)	3	1	2	4
(c)	1	2	3	4
(d)	2	1	4	3

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of assertion.

(c) If assertion is true but reason is false.

(d) If both assertion and reason are false.

35. **Assertion :** For the reaction :
$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$
Rate $= k[CHCl_3][Cl_2]^{1/2}$
Reason : Rate of reaction is always equal to the sum of the stoichiometric coefficients of the reacting species in a balanced chemical equation.

36. **Assertion :** The conductivity of electrolytic solutions increases with increase of temperature.
Reason : Electronic conductance decreases with increase of temperature.

37. **Assertion :** E_a of the forward reaction is higher than that of backward reaction in a reversible endothermic reaction.
Reason : Increasing the temperature of the substance increases the fraction of molecules which collide with energies greater than E_a.

38. **Assertion :** Current stops flowing when $E_{cell} = 0$.
Reason : Equilibrium of the cell reaction is attained.

39. **Assertion :** For a first order reaction, $t_{1/2}$ is independent of rate constant.
Reason : For a first order reaction, $t_{1/2} \propto [R]_0$.

40. **Assertion :** To obtain maximum work from a galvanic cell charge has to be passed reversibly.
Reason : The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy.

SECTION - VI
Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. In a reaction $A \rightarrow$ products, when start is made from 8.0×10^{-2} M of A, half-life is found to be 120 minute. For the initial concentration 4.0×10^{-2} M, the half-life of the reaction becomes 240 minute. The order of the reaction is

42. $Al^{3+}_{(aq)} + 3e^- \longrightarrow Al_{(s)}$; $E° = -1.66$ V

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu(s)$; $E° = +0.34$ V

Voltage produced under standard conditions by combining the half reactions with their respective standard electrode potentials is

43. The rate of formation of a dimer in a second order dimerisation reaction is 9.1×10^{-6} mol dm^{-3} s^{-1} at 0.01 mol dm^{-3} monomer concentration. The rate constant for the reaction is $x \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. Then x is

44. The pH of the half cell solution :
Pt, H_2(1 atm)$|H^+(H_2SO_4)$ is
Given : $E = 0.3$ volt

45. The data given below are for the reaction of NO and Cl_2 to form NOCl at 295 K :

$[Cl_2]$ (mol L^{-1})	[NO] (mol L^{-1})	Initial rate (mol L^{-1} s^{-1})
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

The rate constant of the reaction is x L^2 mol^{-2} s^{-1}. The value of x is

46. The equilibrium constant K for the following cell reaction is

$$Fe^{2+}_{(aq)} + Ag^+_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + Ag_{(s)}$$

$E°_{Fe^{3+}/Fe^{2+}} = +0.77$ V, $E°_{Ag^+/Ag} = +0.80$ V

47. The half life period and initial concentration for a reaction are as follows :

Initial concentration	350	540	158
$t_{1/2}$	425	275	941

The order of the reaction is

48. The equilibrium constant of the reaction :
$Cu_{(s)} + 2Ag^+_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Ag_{(s)}$
$E° = 0.46$ V at 298 K is $x \times 10^{15}$. The value of x is

49. For a first order reaction, the time required for 99% completion is $x \times$ the time required for the completion of 90% of reaction. Then x is

50. The emf of the cell corresponding to the reaction :
$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)}$ (0.1M) $+ H_{2(g)}$ (1atm)
is 0.28 V at 25 °C. The pH of the solution at the hydrogen electrode is x.62, where x is
(Given : $E°_{Zn^{2+}/Zn} = -0.76$ V)

SOLUTIONS

1. **(c) :** Iron coated with zinc does not get rusted even if cracks appear on the surface because Zn will take part in redox reaction not Fe as Zn is more reactive than Fe. If iron is coated with tin and cracks appear on the surface, Fe will take part in redox reaction because Sn is less reactive than Fe.

2. (a) :

	$A \longrightarrow$	B	+	C	+	D
Initial	a	0		0		0
After time t	$a-x$	x		x		x

It is given that $a = P_0$ ... (i)

$a - x + x + x + x = P$

or $a + 2x = P$ ... (ii)

From eqn. (i) and (ii),

$$P_0 + 2x = P \text{ or } x = \frac{P-P_0}{2}$$

From rate equation

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$= \frac{2.303}{t}\log\frac{P_0}{P_0-\left(\frac{P-P_0}{2}\right)} = \frac{2.303}{t}\log\frac{2P_0}{3P_0-P}$$

3. (d): According to Faraday's law of electrolysis

$m \propto Ct$ or $m = ZCt$

where C = current, t = time

$$Z = \frac{\text{Equivalent weight of substance}}{96500}$$

$$\text{Eq. wt. of Cu} = \frac{63.5}{2} \quad (\because\ Cu^{2+} \to Cu)$$

$$Z = \frac{63.5}{2\times 96500}$$

$$\therefore\quad m = \frac{63.5\times C\times t}{2\times 96500} = \frac{31.75\times C\times t}{96500}$$

4. (c) : Catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence, lowering the potential energy barrier.

5. (b): Weight of Ag required

$= 80 \times 5 \times 10^{-3} \times 1.05$ (wt. $= V \times d$)

$= 0.42$ g

$$\because\ W = \frac{EIt}{96500},\quad \therefore\ 0.42 = \frac{108\times 3\times t}{96500}$$

$\therefore\quad t = 125$ sec

6. (b): In the rate law expression, rate $= k[X][Y]^2$

If Y is reduced to one-fourth, the rate of reaction will be 1/16 time of the original rate.

7. (d) : $E = E^\circ + \dfrac{0.591}{n}\log[M^{n+}]$

Lower the concentration of M^{n+}, lower is the E.

8. (c) : $k = \dfrac{1}{24}\ln\dfrac{a}{a/8} = \dfrac{1}{24}\ln 8$

$$= \frac{1}{24}\ln 2^3 = \frac{1}{8}\ln 2\ s^{-1}$$

9. (c) : $\Delta G^\circ = -nFE^\circ$ ... (i)

$\Delta G^\circ = -2.303\ RT\log K$ ... (ii)

From equation (i) if E° is positive, then ΔG° is negative.

In equation (ii), ΔG° is negative

so, $\log K > 0 \Rightarrow K > 1$

10. (a)

11. (c) : Conductivity depends upon solvation of ions present in solution. Greater the solvation of ions, lesser is the conductivity.

12. (a) : $r = k[A]$

$$\therefore\quad k = \frac{10^{-2}}{0.2} = 5\times 10^{-2}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5\times 10^{-2}} = 13.86 \text{ min} = 832 \text{ sec}$$

13. (b): $AB = AC + BD - CD$

$= 91 + 426.2 - 126.5$

$= 390.7\ \text{ohm}^{-1}\ \text{cm}^2\ \text{g-eqiv}^{-1}$

14. (c) : Units of k for second order reaction is $L\ mol^{-1}\ s^{-1}$.

15. (b): $E^\circ = E^\circ_{(cathode)} - E^\circ_{(anode)}$

$= -0.44 - (-0.76) = -0.44 + 0.76$

$= +0.32$ V

16. (b): $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{14.26\times 60}\ \text{sec}^{-1}$

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \text{ (For first order reaction)}$$

$$\frac{0.693}{14.26\times 60} = \frac{2.303}{50}\log\frac{a}{a-x}$$

$$\log\frac{a}{a-x} = \frac{0.693\times 50}{14.26\times 60\times 2.303} = 0.0175$$

$$\frac{a}{a-x} = 1.041$$

$$\text{or}\quad \frac{a-x}{a} = 0.96 \text{ or } 1-\frac{x}{a} = 0.96$$

$$\frac{x}{a} = 0.04 = 4\%$$

17. (a) : Lower the value of reduction potential, stronger will be the reducing agent thus I^- is strongest reducing agent. Higher the value of reduction potential, stronger will be the oxidising agent, thus strongest oxidising agent is F_2.

18. (c) : For the reaction : $2A + B_2 \longrightarrow 2AB$,

Rate $\propto [A]^x[B_2]^y$. On substituting the given data, we get

From experiment 1,

$$1.6 \times 10^{-4} \propto (0.50)^x (0.50)^y \qquad \ldots \text{(i)}$$

From experiment 2,

$$3.2 \times 10^{-4} \propto (0.50)^x (1.00)^y \qquad \ldots \text{(ii)}$$

From experiment 3,

$$3.2 \times 10^{-4} \propto (1.00)^x (1.00)^y \qquad \ldots \text{(iii)}$$

On dividing equation (ii) by (i), we get

$$2 = \left(\frac{1.00}{0.50}\right)^y$$

or, $2 = 2^y$ or $2^1 = 2^y$ or $y = 1$

On dividing equation (iii) by (ii), we get

$$1 = \left(\frac{1.00}{0.50}\right)^x$$

or, $1 = 2^x$ or $2^0 = 2^x$ or $x = 0$

Rate $= k[A]^0[B_2]^1 = k[B_2]$

19. (a) : $\lambda^\circ_{HCOOH} = \lambda^\circ_{H^+} + \lambda^\circ_{HCOO^-}$

$= 349.6 + 54.6$

$= 404.2\ S\ cm^2\ mol^{-1}$

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{46.1}{404.2} = 0.114 \text{ or } 11.4\%$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{1-0.114}$$

$$= \frac{0.025 \times 0.114 \times 0.114}{0.886}$$

$$= 3.67 \times 10^{-4}$$

20. (c) : The order of a reaction may or may not be equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.

21. (a) : As Cu is below hydrogen in the electrochemical series, hydrogen is oxidised at anode and comes out as H_2 while Cu is reduced at the cathode.

$2H^+ + 2e^- \longrightarrow H_2, E^\circ = 0.0$ volt

$Cu^{2+} + 2e^- \longrightarrow Cu, E^\circ = 0.337$ volt

22. (a, b) : (a) and (b) are correct. (c) is wrong because frequency factor gives total number of collisions and not effective collisions. (d) is wrong because half-life of the reaction decreases with increase of temperature (as reaction becomes faster).

23. (b, c, d) : Cathode : $Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$

$Fe^{3+}_{(aq)} + 3e^- \longrightarrow Fe_{(s)}$

Anode (in all the three cases) :

$H_2O_{(l)} \longrightarrow 2H^+_{(aq)} + 1/2\ O_{2(g)} + 2e^-$

24. (b, d) : $\dfrac{k_{T+10K}}{k_T} = \exp\left(\dfrac{(10\text{ K})E_a}{RT(T+10\text{ K})}\right)$

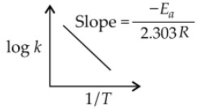
A plot between $\ln k$ and $\dfrac{1}{T}$ gives straight line.

25. (a, b, d) : Those metals will be oxidized by NO_3^- ion whose oxidation potentials are more than that of NO_3^- ion or whose reduction potentials are less than that of NO_3^- ion. These are V^{2+}, Fe^{3+} and Hg^{2+}. Hence, the metals oxidized will be V, Fe and Hg.

26. (c) : Arrhenius equation is

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

Comparing with $y = c + mx$



27. (d) : According to Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\log k = \log A - \frac{E_a}{2.303RT} \qquad \cdots \text{(i)}$$

For a first order reaction, $t_{1/2} = \dfrac{0.693}{k}$

$t_{1/2} = 10$ min $= 600$ s

$$\therefore \quad k = \frac{0.693}{600} = 1.1 \times 10^{-3}\ s^{-1} \qquad \cdots \text{(ii)}$$

Putting (ii) in (i) we get,

$\log(1.1 \times 10^{-3})$

$$= \log(4 \times 10^{13}) - \frac{98.6 \times 10^3}{2.303 \times 8.314 \times T}$$

$\therefore \quad T = 310.9$ K

28. (c) : $k_1 = A_1 e^{-E_{a_1}/RT}$

$k_2 = A_2 e^{-E_{a_2}/RT}$

$k_3 = A_3 e^{-E_{a_3}/RT}$

Since, $k = \frac{k_1 k_3}{k_2} = \left(\frac{A_1 A_3}{A_2}\right) e^{-(E_{a_1}+E_{a_3}-E_{a_2})/RT}$

$\therefore \quad E_a = E_{a_1} + E_{a_3} - E_{a_2}$

$= 50 + 30 - 40 = 40$ kJ

29. (c) : Molar conductivity increases with dilution because the total volume of the solution containing 1 mole of electrolyte increases.

30. (b): Electrolyte X is strong electrolyte as on dilution the number of ions remains same, only interionic attraction decreases and hence not much increase in Λ_m is seen.

While Y is a weak electrolyte since, Λ_m for a weak electrolyte like CH_3COOH increases significantly on dilution.

31. (a) : Specific conductivity decreases because number of ions per unit volume decreases on dilution.

32. (c) : $MnO_4^- = 96500 \times 5$ F $= 482500$ C

$Cr_2O_7^{2-} = 96500 \times 6$ F $= 579000$ C

$Fe^{3+} = 96500 \times 1$ F $= 96500$ C

$Cl_2 = 96500 \times 2$ F $= 193000$ C

33. (b)

34. (d): (P) For strong electrolytes, Λ_m and molarity (C) are related by Onsager's eq. as

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$$

A plot of Λ_m *vs* $\sqrt{C}$ (abscissa) would be a straight line with intercept on y-axis $= \Lambda_m^\circ$

(Q) For weak electrolytes (like C_2H_5COOH), Λ_m *vs* $\sqrt{C}$ is a curve which cannot be extrapolated to $C = 0$.

From Kohlrausch law,

$$\Lambda^\circ_{C_2H_5COOH} = \Lambda^\circ_{C_2H_5COO^-} + \Lambda^\circ_{H^+}$$

35. (c) : Rate of reaction depends upon the experimental conditions such as concentration of reactants, temperature and catalyst.

36. (b): Conductivity of electrolytic solutions depends upon the ions produced in solution which increases with increase of temperature. (ionization increases).

37. (b): Threshold energy of reactants is less than that of products in reversible endothermic reactions, hence, E_a for forward reaction is more than E_a for backward reaction.

38. (a)

39. (d): For a first order reaction half life period is constant *i.e.* it is independent of initial concentration of the reacting species. It is related to rate constant as

$$t_{1/2} = \frac{0.693}{k}$$

40. (a) : Electrical work done in one second is equal to electrical potential multiplied by total charge passed and is related to Gibb's energy of the reaction as follows :

$$\Delta_r G = -nFE_{cell}$$

41. (2) : $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$; $\frac{120}{240} = \left(\frac{4\times10^{-2}}{8\times10^{-2}}\right)^{n-1}$; $n = 2$

42. (2) : The cell will be

$Al_{(s)} \mid Al^{3+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$

$E_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Al^{3+}/Al}$

$= +0.34 - (-1.66)$

$= +2.00$ V

43. (9) : Let the second order dimerisation reaction be

$$2A \rightarrow A_2$$

Rate of formation of dimer $= k[A]^2$

$\therefore \quad k = \frac{\text{Rate of formation of dimer}}{[A]^2}$

$= \frac{9.1\times10^{-6}}{(0.01)^2}$

$= 9.1 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}

$\approx 9 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} $\quad \therefore \quad x = 9$

44. (5) : $E_{H_2|H^+} = E^\circ_{H_2|H^+} - \frac{0.0591}{2}\frac{\log[H^+]^2}{p_{H_2}}$

$$= 0.0 - 0.0591\log\frac{[H^+]}{1}$$

$0.3 = 0.0591$ pH $\quad [\because \text{pH} = -\log[H^+]$

pH ≈ 5

45. (8) : For the reaction :

$$2NO + Cl_2 \longrightarrow 2NOCl$$

Rate $= k[Cl_2]^m[NO]^n$

where m and n are order of the reaction w.r.t. Cl_2 and NO.

$\therefore \quad 1 \times 10^{-3} = k(0.05)^m(0.05)^n \quad \ldots$ (i)

$3 \times 10^{-3} = k(0.15)^m(0.05)^n \quad \ldots$ (ii)

$9 \times 10^{-3} = k(0.05)^m(0.15)^n \quad \ldots$ (iii)

From equations (i) and (ii) we get; $m = 1$

From equations (i) and (iii) we get; $n = 2$

$\therefore$ Overall order is 3; with respect to Cl_2 it is 1 and with respect to NO is 2.

$\therefore \quad 1 \times 10^{-3} = k(0.05)(0.05)^2$

$$k = \frac{1\times10^{-3}}{1.25\times10^{-4}}$$

$k = 8\ L^2\ mol^{-2}\ s^{-1}$

$\therefore \quad x = 8$

46. (3) : $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= +0.80 - (+0.77) = 0.03$ V

Equilibrium constant, $K = \text{antilog}\left(\frac{nE^\circ}{0.059}\right)$

$$= \text{antilog}\left(\frac{1\times0.03}{0.059}\right) = 3.224 \approx 3$$

47. (2) : $t_{1/2} \propto (a)^{1-n}$

where n is the order of a reaction.

For I, $\quad 425 \propto (350)^{1-n} \quad \ldots$ (i)

For II, $\quad 275 \propto (540)^{1-n} \quad \ldots$ (ii)

For III, $\quad 941 \propto (158)^{1-n} \quad \ldots$ (iii)

By eqs. (i) and (ii), $\frac{425}{275} = \left(\frac{350}{540}\right)^{1-n}$

Taking log,

$$\log\frac{425}{275} = (1-n)\log\left(\frac{350}{540}\right)$$

$\therefore \quad n = 2$

48. (4) : $K = \text{antilog}\left(\frac{nE^\circ}{0.059}\right)$

$= \text{antilog}\left(\frac{2\times0.46}{0.059}\right)$

$= \text{antilog}\ (15.593)$

$= 3.9 \times 10^{15}$

$\approx 4 \times 10^{15}$

$\Rightarrow \quad x = 4$

49. (2) : Let the time for 90% completion and 99% completion are denoted by $t_{0.90}$ and $t_{0.99}$ respectively.

The kinetic equation for first order reaction is,

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

For 99% completion,

$$k = \frac{2.303}{t_{0.99}}\log\left(\frac{100}{100-99}\right) = \frac{2.303}{t_{0.99}}\times 2 \quad \ldots \text{(i)}$$

For 90% completion

$$k = \frac{2.303}{t_{0.90}}\log\left(\frac{100}{100-90}\right) = \frac{2.303}{t_{0.90}}\times 1 \quad \ldots \text{(ii)}$$

Equating (i) and (ii) we get, $t_{0.99} = 2 \times t_{0.90}$

$\therefore \quad x = 2$

50. (8) : At anode :

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-; E^\circ_{Zn^{2+}/Zn} = -0.76$ V

At cathode : $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}; E^\circ_{SHE} = 0.00$ V

$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}; E^\circ = 0.76$ V

$$K = \frac{[Zn^{2+}][H_2]}{[Zn][H^+]^2} = \frac{0.1\times1}{[H^+]^2}$$

$E^\circ = E^\circ_{cathode} - E^\circ_{anode}$

$= E^\circ_{H^+/H_2} - E^\circ_{Zn^{2+}/Zn}$

$= 0 - (-0.76) = 0.76$ V

$\therefore \quad E = E^\circ - \frac{0.0591}{n}\log K$

$$0.28 = 0.76 - \frac{0.0591}{2}(\log 0.1 - 2\log[H^+])$$

$$0.48 = \frac{0.0591}{2}(-1 + 2\,\text{pH}) \quad (\because -\log[H^+] = \text{pH})$$

$\therefore \quad$ pH $= 8.62$, $x = 8$

YOU ASKED WE ANSWERED

Do you have a question that you just can't get answered?

Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

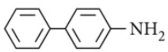
The best questions and their solutions will be printed in this column each month.

Q1. What are the chemicals present in hair dyes that are known to be carcinogenic?

– Ruchi Yadav, Mysore

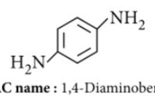
Ans. There are many chemicals present in the hair dye. A few chemicals that you should try to avoid if you are thinking of dying your hair are *o*- and *m*-toluidines, *p*-phenylenediamine, persulphates, resorcinol, hydrogen peroxide, ammonia, lead acetate, 4-ABP.

4-Aminobiphenyl is an amine derivative of biphenyl which is used in manufacture of azo dyes. It is a known human carcinogen.



IUPAC name : 4-Aminobiphenyl
Other name : 4-ABP

Another carcinogenic compound is *p*-phenylenediamine (PPD) which is also an ingredient of semi-permanent hair colour. It is a white solid, but can darken due to air oxidation.



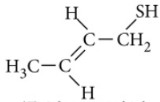
IUPAC name : 1,4-Diaminobenzene
Other name : *p*-Phenylenediamine or 1,4-Phenylenediamine

Q2. What is 'Skunk spray' ? Give its chemical composition.

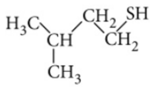
– Lalit Shrivastava, Patna

Ans. Skunk is a pretty black cat with the white stripe down its back and is common in suburban areas. Skunks are notorious for their anal scent glands, which they use as a defensive weapon. These glands produce a mixture of sulphur containing chemicals such as thiols, also called mercaptans, which have a highly offensive smell.

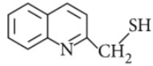
'Skunk spray' is composed mainly of three low-molecular-weight thiol compounds, (*E*)-2-butene-1-thiol, 3-methyl-1-butanethiol, and 2-quinoline methanethiol, as well as acetate thioesters of these. These compounds are detectable by the human nose at concentrations of only 10 parts per billion.



(*E*)-2-butene-1-thiol



3-methyl-1-butanethiol



2-quinoline methanethiol

Q3. Which chemical is used for marking people's fingers during elections? Why does it not rub off?

–Meenakshi Sahani, Delhi

Ans. Silver nitrate is the basic component used in the election ink. The ink is violet in the bottle and turns black when dabbed on a finger. When the ink is applied, it reacts with the oxides of chlorine present in our skin and postures to form silver chloride which is insoluble in water and as we known that AgCl is unstable in contact of UV rays or UV light, it forms metallic silver layer that is combined with the epidermal layer of our skin and cannot be removed.

$$\underset{\text{(Soluble in water)}}{AgNO_3} + NaCl \longrightarrow \underset{\text{(Insoluble in water)}}{AgCl} + NaNO_3$$

$$AgCl \xrightarrow{UV} \underset{\text{(Metallic silver)}}{Ag}$$

$$Ag + \underset{\text{(Present in air)}}{2S} \longrightarrow \underset{\text{(Black)}}{Ag_2S}$$

As new skin grows and the old skin sloughs off, the ink stain will disappear. The ink on the skin goes off in a week. The ink on the nail takes longer, as the nail grows out.

CHEMISTRY MUSING

SOLUTION SET 11

1. **(d):** Let n be the no. of moles of gas.

$$\therefore \quad n = \frac{PV}{RT} = \frac{1.6\times10^6\times0.0083}{8.3\times300} = 5.33$$

Given that, $C_p = \frac{5}{2}R$

As $\quad C_p = C_v + R$

$\therefore \quad C_v = C_p - R$

$$C_v = \frac{5}{2}R - R = \frac{3}{2}R = \frac{3}{2}\times 8.3$$
$$= 12.45\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$q_v = n\times C_v \times \Delta T$$

$\Rightarrow \quad 2.49\times10^4 = 5.33\times12.45\times\Delta T$

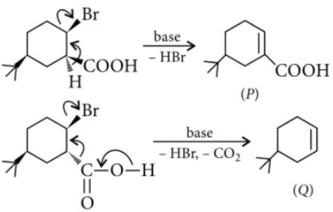
$\therefore \quad \Delta T = 375$ K

$\therefore \quad T_f = 300 + 375 = 675$ K

$$P = \frac{nRT}{V} = \frac{5.33\times8.3\times675}{0.0083} = 3.59\times10^6\ \text{N/m}^2$$

2. **(a):** (II) Trihalides of group 15 elements are predominantly covalent with the ionic character increasing down the group. Thus, NF_3 and PF_3 are covalent while BiF_3 is ionic.
(IV) Stability of hydrides of carbon family decreases down the group due to weak M—H bond. Thus, stability decreases in the order :
$$CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$$

3. **(c):** Anti-elimination via E2 mechanism takes place in presence of strong bases as follows :



4. **(c)**

5. **(c):** If one of the ions (either cation or anion) is very big, the solubility increases with decreasing the size of other ion.

CsF > CsCl > CsBr > CsI (very big cation, Cs^+)
$LiNO_3 > NaNO_3 > KNO_3 > CsNO_3$ (very big anion, NO_3^-)

Also, greater the charge on cation or anion, lower will be the solubility.

$$\xrightarrow[\text{Charge on cation increases, solubility decreases}]{Na^+Cl^- \quad Ba^{2+}(Cl^-)_2 \quad Al^{3+}(Cl^-)_3}$$

$$\xrightarrow[\text{Charge on anion increases, solubility decreases}]{Na^+Cl^- \quad (Na^+)_2SO_4^{2-} \quad (Na^+)_3PO_4^{3-}}$$

6. **(a):** $y_A = \dfrac{p_A}{p_A + p_B} = \dfrac{x_A p_A^\circ}{x_A p_A^\circ + x_B p_B^\circ}$

By putting $x_B = 1 - x_A$, we get

$$\frac{1}{y_A} = \frac{p_B^\circ}{p_A^\circ}\frac{1}{x_A} + \frac{p_A^\circ - p_B^\circ}{p_A^\circ} \qquad (y = mx + c)$$

Hence, plot of $1/y_A$ along y-axis versus $1/x_A$ along x-axis will be straight line with slope $= p_B^\circ/p_A^\circ$.

7. **(a):** Rate of reaction towards S_N1 reaction :
$$\underset{\text{(fastest)}}{3°} > 2° > 1° > \underset{\text{(slowest)}}{\overset{+}{C}H_3}$$
Greater the stability of carbocation, faster will be the reaction. $C_6H_5CH_2-\overset{+}{C}(CH_3)-CH_2CH_3$ is most stable *tert*. carbocation.

8. **(c):** $Ph-\overset{*}{C}(CH_3)(H)-I$ has one chiral C-atom and is optically active. Thus, the product formed will be a racemic mixture via S_N1 mechanism in polar protic solvent, C_2H_5OH.

9. **(7):** Energy per photon $= \dfrac{hc}{\lambda}$

$$= \frac{6.626\times10^{-34}\times3.0\times10^8}{0.57\times10^{-6}\,\text{m}} = 3.487\times10^{-19}\ \text{J}$$

Watt = No. of photons emitted per sec × Energy per photon ($\because$ Watt = 25 J s^{-1})

$25 = \text{No. of photons} \times 3.487\times10^{-19}$

No. of photons emitted $= 7.168\times10^{19}\ s^{-1}$

10. **(4):** $[Co(ox)_3]^{3-}$: d^2sp^3; inner orbital complex
$[Fe(H_2O)_6]^{3+}$: sp^3d^2; outer orbital complex
$[Ni(NH_3)_6]^{2+}$: sp^3d^2; outer orbital complex
$[Mn(CN)_6]^{4-}$: d^2sp^3; inner orbital complex
$[Cr(H_2O)_6]^{3+}$: sp^3d^2; outer orbital complex
$[CoF_6]^{3-}$: sp^3d^2; outer orbital complex
$[Fe(CN)_6]^{3-}$: d^2sp^3; inner orbital complex.